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The Constitution of Iron–Nickel–Chromium Alloys at 550–800° C.

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SYNOPSIS

The paper gives the results obtained from a metallographic and X-ray examination (including lattice parameter measurements) of a series of high-purity iron–nickel–chromium alloys in an attempt to establish the equilibrium constitution at 550° C., with particular reference to the development of sigma phase in the alloy system. The range of alloys investigated contained from 0–40% of nickel and 0–35% of chromium. The alloys were heat-treated for periods of up to 700 days at 550° C., but owing to the persistence of the metastable alpha phase in alloys containing more than 20% of nickel, the phase boundaries beyond this limit have not been definitely fixed.

Additional work on the constitution of iron–nickel–chromium alloys at 650° and 800° C. has enabled certain details of the constitution at these temperatures to be fixed with more certainty.

Introduction

IRON–NICKEL–CHROMIUM alloys form the basis of numerous industrial heat-resisting steels and alloys for high-temperature service, and for this reason a number of investigators[1, 2] have reported on the constitution of the Fe–Ni–Cr system at various temperatures. Attention has been given more recently to those portions of the constitution diagrams, within the ranges of nickel and chromium concentrations commonly used in corrosion- and heat-resisting alloys, in which sigma may be formed at service temperatures.[3, 4, 5]

The formation of σ in these alloys, accompanied by changes in their mechanical properties, has been known for some years, and their possible use for gas-turbine components increases the importance of knowing the constitution of the Fe–Ni–Cr system at temperatures between 550° and 800° C. The composition range over which σ is found at 650° and 800° C. in alloys containing up to about 60% of nickel and 50% of chromium has been previously determined at the National Physical Laboratory,[5] and the present paper deals mainly with an investigation of the constitution of the same alloys at 550° C. Although austenitic steel components are generally chosen when the service temperature is above 550° C., the use of cooling devices often ensures that some parts of the components are well below 550° C. Below 550° C. changes within the alloy are very slow—in the present work annealings of two years did not always achieve complete equilibrium—and it is thought that cases in which the austenite loses more chromium than is indicated by the diagram for equilibrium at 550° C. will be rare in practice.

The results previously published describing the equilibrium at 650° and 800° C. showed certain discrepancies between the X-ray and microscopic observations. Some further work is described in which the points of difference have been examined; it is thought that the results of the two methods of investigation have now been brought to agreement.

CONSTITUTION AT 550° C.

Experimental Methods

The compositions of the alloys, which with a few exceptions were the same as those used in the previous work,[5] are given in Table I.* They were prepared from high-purity iron, nickel, and chromium by melting under dry hydrogen in thoria-lined alumina

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* Throughout the paper the reference numbers are used to indicate the nominal composition of the alloys in wt.-%; thus 5*F*22 represents an alloy nominally containing 5% of nickel, 22% of chromium, and the balance iron.

Table I

CHEMICAL ANALYSIS OF ALLOYS

Alloy	Ni, %	Cr, %	Fe, %	Other Elements, %
8*F*18	8·12	18·31	ND	
8*F*20	8·09	20·22	ND	
9*F*20	8·64	19·86	71·30	N_2 0·008
11*F*40	11·25	40·40	48·37	Insol. 0·07
12*F*20*	11·27	21·18	67·45	Insol. 0·05, Si Nil
12*F*19	12·84	18·40	ND	
13*F*18	13·36	17·20	69·23	
13*F*45	13·30	48·52	38·16	
14*F*15*	14·47	15·19	70·25	Insol. 0·03
14*F*20	14·26	18·96	ND	C 0·004
14*F*28	15·30	27·82	56·82	Insol. 0·07, Si 0·002
16*F*11	16·02	10·76	72·94	
17*F*23	16·72	22·91	60·20	
19*F*30	19·10	33·20	48·30	
18*F*5*	17·99	5·03	76·94	
19*F*20*	19·51	19·36	61·01	
20*F*25	20·16	24·65	ND	C 0·006
21*F*17	21·07	16·41	62·65	
23*F*14*	23·34	14·71	62·01	
23*F*25*	23·90	27·00	49·10	Insol. 0·05, C 0·0045
26*F*24	26·33	22·83	50·75	
26*F*26	25·13	26·07	48·72	Insol. 0·07
26*F*27	26·10	27·08	ND	
26*F*31	26·43	31·24	42·19	
27*F*37	27·27	39·05	33·62	Insol. 0·06
30*F*19	29·87	18·93	ND	
30*F*23	30·01	23·00	ND	
30*F*31	29·60	30·20	ND	
31*F*26	31·25	25·78	42·77	N_2 0·004, Si 0·006
32*F*14	30·78	13·97	ND	
33*F*33*	34·01	33·24	32·69	Insol. 0·06
35*F*12	36·90	12·40	50·90	
35*F*22	35·29	22·05	42·42	N_2 0·004, Si 0·004
37*F*29	36·47	29·68	ND	
38*F*18	38·34	18·22	ND	
41*F*16	40·88	16·75	42·21	
41*F*24	41·58	22·40	ND	
42*F*23	42·29	23·00	ND	C 0·002
45*F*19	44·86	19·96	ND	
48*F*22	50·90	20·50	28·60	Insol. 0·07
50*F*30	50·04	30·07	ND	
0*F*30*	...	28·70	ND	
0*F*32	...	32·46	ND	
0*F*38	...	38·72	ND	
1*F*20	0·95	19·82	79·06	
1*F*25	1·10	26·34	72·42	
1*F*30	1·16	30·72	67·82	
2*F*20	2·24	22·48	74·98	
2*F*25	2·02	24·48	73·38	
2*F*28	2·07	27·08	70·63	
3*F*18	3·03	17·36	79·40	
3*F*20	3·07	19·18	77·65	
3*F*25	3·00	24·56	72·27	
4*F*25	4·33	25·00	ND	
5*F*18	5·10	17·80	ND	
5*F*20	5·08	20·40	ND	
5*F*22	4·84	21·80	ND	
5*F*30	4·99	29·68	ND	
5*F*34	5·45	33·63	ND	
5*F*38	4·98	36·97	58·24	
6*F*30	6·40	30·10	ND	
6*F*35*	6·73	34·94	58·09	Insol. 0·05, Si Nil
9*F*37*	10·13	38·27	51·42	
20*F*0*	20·43	...	79·61	
31*F*0*	33·94	...	66·12	
35*F*25	34·70	25·80	ND	C 0·003

N.D. = Not determined

* Alloys made by melting previously deoxidized metals *in vacuo*; all other alloys were made by melting in dry purified hydrogen

crucibles in an induction furnace. Full details of the melting technique are given in the paper by Rees, Burns, and Cook.[5] The ingots were homogenized at 1350° C. for three days and quenched from 1000° C., after which:

(i) Lump samples from the ingots were annealed at 550° C. for times up to 590 days and subjected to periodical microscopic examination

(ii) Powder samples for X-ray examination by the Debye-Scherrer method were annealed in evacuated silica tubes for times up to 700 days

(iii) Small slices from the ingots were alternately cold-rolled to about 50% reduction and annealed at 550° C. until no further change took place. It had previously been found that the rate at which the σ constituent was precipitated at 650° C. could be increased about a thousand times if the alloy was severely cold-worked before annealing.

All samples were annealed in evacuated silica tubes and quenched from the annealing temperature. Solid samples were quenched by breaking the silica capsules under water, but the powder containers were immersed in water without exposing the powders.

Examination of Alloys Annealed at 550° C.

Four research laboratories—the National Physical Laboratory, Brown-Firth Research Laboratories, the Metallurgical and Research Department of the English Steel Corporation, and the Central Research Laboratories of the United Steel Companies, Ltd.—have co-operated in the microscopic and X-ray examination of the alloys listed in Table I (after long periods of annealing at 550° C.). The results of these examinations are given in Tables II–V, and are summarized and assessed in Table VI.

Microstructures

The general form of the equilibrium diagram of the alloys for the temperature of the initial annealing and at the lower temperatures with which the study is concerned is given in *Metals Handbook*.[6]

After being quenched from 1000° C. the alloys consisted either of ferrite alone, or austenite alone, or of mixtures of ferrite and austenite. In alloys which were strain-free and single-phase before annealing at 550° C., the amount of second phase formed during annealing was very small, and in many cases no precipitate formed, although examination of cold-worked and annealed samples showed that the alloys should be duplex after treatment at 550° C. An increased amount of precipitate occurred in the alloys that were cold-worked before annealing, but the precipitate was in the form of very fine particles, which were difficult to identify. In general the σ was more rapidly attacked than either α or γ when etched electrolytically in oxalic acid, or in a mixture of *aqua regia* and glycerine, and this effect has been used for distinguishing σ among these constituents. When the precipitate was coarse, as in the initially duplex alloys, the coloration obtained with a solution of alkaline ferricyanide (modified Murakami's reagent) was used to distinguish σ, this phase acquiring a dark-red colour after etching at 70° C. for 5–10 sec. There was, however, no etching technique available that would infallibly distinguish between finely precipitated sigma, alpha, and gamma.

Ferritic Alloys

Many of the alloys which were entirely ferritic after quenching from 1000° C. easily became passive, and interpretation of their structures after annealing was difficult. Cold-working accelerated the precipitation of second or third phases as very fine particles. Figure 1 shows the structures of an alloy containing about 5% of Ni and 22% of Cr (5*F*22) after annealing strain-free specimens at 550°, 650°, and 800° C. Precipitation at each temperature had occurred along crystallographic planes, but it was not possible to state whether the precipitate at 550° C. consisted of both γ and σ. The marked effect of cold-working before annealing on the fineness of the structure can be seen in Fig. 2*a*; the more rapid etching of the σ in this case (3*F*20) enabled it to be distinguished from the γ-phase. In another alloy containing 6% of Ni and 30% of Cr (Fig. 2*b*) the proportion of the precipitated phases was so high as to render a clear differentiation between γ and σ more difficult. In this alloy the precipitation was exceptionally dense along certain crystallographic planes. No precipitate was observed at 550° C. in a 30% Cr alloy containing 1% of Ni; precipitate was found in alloys containing 22–25% of Cr and 3–5% of Ni, and this was thought to be γ alone in the lump specimens, although X-ray examination of the powder samples showed the presence of σ also.

Alloys Consisting of Austenite and Ferrite before Annealing

In strain-free alloys consisting of austenite and ferrite before annealing, the formation of σ was very slow, and began in the ferrite areas. Figure 3*a* shows the structure of alloy 12*F*20 after 574 days, in which the ferrite areas were completely altered and the austenite areas were unchanged. In one area of this specimen the small amount of cold-work caused by a stamp mark was sufficient to cause breakdown of the γ matrix; this is shown in Fig. 3*b*. In cold-worked samples complete decomposition occurred in both the ferrite and austenite areas, producing structures such as that in Fig. 4*a*, in which it was difficult to distinguish which particles were σ and which were α. Another cold-worked sample of the alloy shown in Fig. 4*a*, annealed for a slightly shorter time, yielded definite evidence of σ (Fig. 4*b*). The austenite areas in alloys containing about 9% of Ni and 20% of Cr had a slightly acicular structure, indicating that some transformation to the α_2 structure (distorted alpha) had taken place during quenching from the annealing temperature. This acicular structure is shown in Fig. 4*b*.

Alloys Consisting of Austenite before Annealing

No alloy consisting entirely of austenite in the strain-free condition showed any precipitated particles in the centre of the austenite grains after the long treatments at 550° C. Those alloys which consisted of γ and σ at 650° C., and which would consequently have been expected to be also in the two-phase field at 550° C., showed only a slight precipitation in the austenite grain boundaries. Figure 5, a photomicrograph of an alloy with 12% of Ni and 19% of Cr after 535 days at 550° C., is an example. Similar alloys which had been cold-rolled before annealing showed a uniform dispersion of fine rounded particles (Fig. 6). In alloys with nickel contents of higher than 20%, not only was the rate of formation of a second phase retarded, but removal of the effects of cold deformation was also slow. Figure 7*a* shows that in an alloy containing 35% of Ni and 22% of Cr the elongated deformed structure was still visible after 84 days' annealing. After 570 days it had been replaced by the structure shown in Fig. 7*b*. The rounded particles in this case could not be identified with certainty as σ or α, but in the case of a similar alloy containing 30% of Ni, repeated electrolytic etching in oxalic acid darkened some of the precipitated particles and others remained unattacked; it

Table II

ALLOYS TREATED AT 550° C. AND EXAMINED AT BROWN-FIRTH LABORATORIES

Alloy	Condition before Treatment	Microscopic Examination of Lump Samples		X-Ray Examination of Metal Powder Samples*		
		Microstructure and Probable Constitution	Time, days	Phases Identified	Time, days	Lattice Parameter of γ Phase, kX
3*F*18	α strain-free	Interpretation doubtful on account of difficulty in etching samples	524	α + γ + σ	590	Weak σ†
3*F*20	α strain-free		524	α + γ + σ	590	Very weak γ, weak to medium σ†
5*F*20	α + trace of γ; strain-free	γ (or α_2) + α	524	α + γ + σ	590	α lines diffuse†
5*F*22	α strain-free	γ (or α_2) + α	524	α + γ + σ	590	As above†
20*F*25	γ (powder only)	...		γ + σ	596	3·5777, very weak σ
30*F*23	γ cold-worked	α (possibly also σ) may have precipitated on the crystallographic planes of the γ. Recrystallization may have involved coalescence of this precipitate	218	γ + α	218	3·5755, α very weak
35*F*25	γ cold-worked		218	γ + α	218	3·5743, α weak
37*F*29	γ cold-worked		218	γ + α	218	3·5733, α weak to medium
41*F*24	γ strain-free		518	γ + α	450	3·5723, α very weak

γ strong

* Metal powders annealed in cold-worked condition
† No lattice parameter determined for these alloys

was considered that both α and σ might have been present. The results of X-ray examination of powder specimens, however, indicated that σ was not formed in any alloy containing more than 21% of Ni.

X-Ray Examination

The X-ray examination of the powder samples was carried out at the National Physical Laboratory in a 9-cm. powder camera using unfiltered chromium radiation. The United Steel Companies' Research Laboratory used originally a 9-cm. camera and unfiltered cobalt radiation, but, finding this unsatisfactory for accurate parameter measurements of the γ-phase, changed to chromium radiation and a 19-cm. camera. Brown-Firth's Research Department also used cobalt radiation and a 19-cm. camera, but employed manganese radiation for parameter determinations. The wavelengths of characteristic X-radiations used for the determination of lattice parameters were:

$CrK\alpha_1$	2·28503 kX	$MnK\alpha_1$	2·09751 kX
$CrK\alpha_2$	2·28891 kX	$MnK\alpha_2$	2·10149 kX
$CrK\beta_1$	2·0806 kX	$MnK\beta_1$	1·90620 kX

Each of the co-operating research laboratories estimated the parameter measurements to be accurate to ± 0·0002 kX. A mean correction for room-temperature variation using the known coefficient of expansion of austenitic steels was applied to the N.P.L. measurements in order to standardize the measurements to 20° C., but no correction was applied to the values obtained in the other co-operating laboratories. The order of correction is such that when room temperature rises to 28° C. it amounts to 0·0004 kX. The estimations of relative phase proportions were made from two sets of films taken with cobalt radiation and one set taken with chromium radiation. The sensitivity of detection of the σ is not so high with cobalt as with chromium radiation, so that direct comparison of the amount of σ estimated by the different observers is difficult. On the whole the agreement between the three sets of results was very satisfactory.

The detailed results of the X-ray examination are given in Tables II–VI. The results are in fair agreement with those of the microscopical examination, although there were a few cases in which σ was definitely formed in the X-ray powder samples when the corresponding lump sample appeared to have remained unchanged. In making an assessment of the results of the microscopic and X-ray examination, due weight has been given to positive evidence of the presence of a constituent. Thus, if X-ray examination showed the presence of either α or σ lines in the spectrum of an alloy, and no precipitation was observed in the microstructure, the alloy was considered to be definitely duplex. Examples of alloys which gave this kind of evidence are 1*F*20 and 1*F*25

Table III

ALLOYS TREATED AT 550° C. AND EXAMINED AT ENGLISH STEEL CORPORATION'S LABORATORY (NO X-RAY EXAMINATION)

Alloy	Condition before Treatment	Microscopic Examination of Lump Samples	
		Microstructure and Probable Constitution	Reheating Time, days
2*F*20	α cold-worked	Many small grains of a second constituent produced. Some of these etched to suggest σ (α + γ + σ)	
3*F*20	α cold-worked		84
2*F*25	α cold-worked	Slight traces of a second constituent, identity uncertain	84
5*F*30	α cold-worked	Indication that σ was deposited along cleavage planes and γ in the matrix (α + γ + σ)	84
6*F*30	α cold-worked		
8*F*18	γ + α cold-worked	Decomposition of both phases. Many dark etching particles deposited, σ. Widmanstätten pattern in some areas suggesting γ, α_2 (γ + α + σ)	84
12*F*20	γ + α strain-free	Decomposition of the ferrite was the major reaction. Localized breakdown occurred in some γ areas. No good evidence of σ (γ + α)	574
17*F*23	γ strain-free	Traces of a second constituent in grain boundaries—identity uncertain, α or σ	574
19*F*20	γ strain-free	Similar to 17*F*23 (strain-free)	574
	γ cold-worked	Numerous sub-angular particles of σ formed in γ matrix. This matrix also contained many fine unresolvable particles, probably α (γ + σ + α ?)	84
23*F*25	γ strain-free	Some deposition along grain boundaries; identity uncertain, α or σ	570
26*F*24	γ strain-free	Traces of precipitation in boundaries	574
	cold-worked	Precipitate in boundaries and traces of intragranular precipitate which was deeply etched; identity uncertain, γ + α	574
26*F*26	γ strain-free	Very small amount of deposition along grain boundaries; uncertain whether α or σ	574
31*F*26	γ strain-free	Definite precipitation along grain boundaries; identity uncertain—most probably α	570
35*F*22	γ strain-free	Some precipitation along grain boundaries; identity uncertain—probably α	570
41*F*24	γ cold-worked	Cold-work effects still prominent. Precipitation of very fine particles in strained areas (γ + α)	84

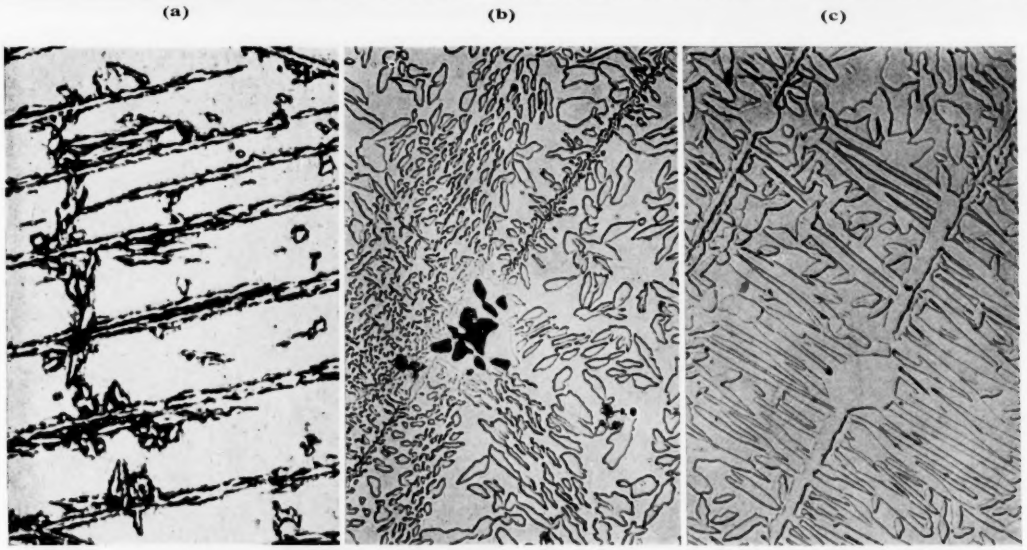

Fig. 1—Alloy **5*F*22** : precipitation at : (***a***) 550° C. $\alpha + \gamma + (\sigma)$; (***b***) 650° C. $\alpha + \gamma + \sigma$; (***c***) 800° C. $\alpha + \gamma$ × 500

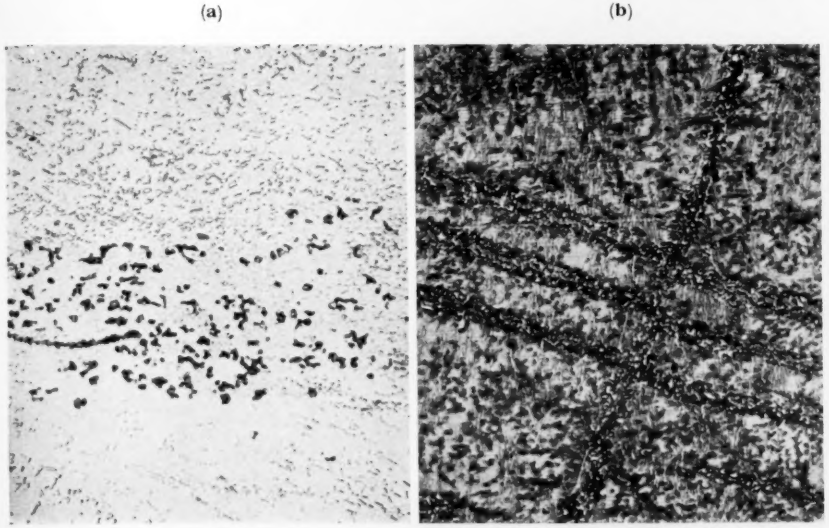

Fig. 2—Alloys cold-rolled, annealed at 550° C. for 84 days, showing $\alpha + \gamma + \sigma$: (***a***) **3*F*20** ; (***b***) **6*F*30** × 500

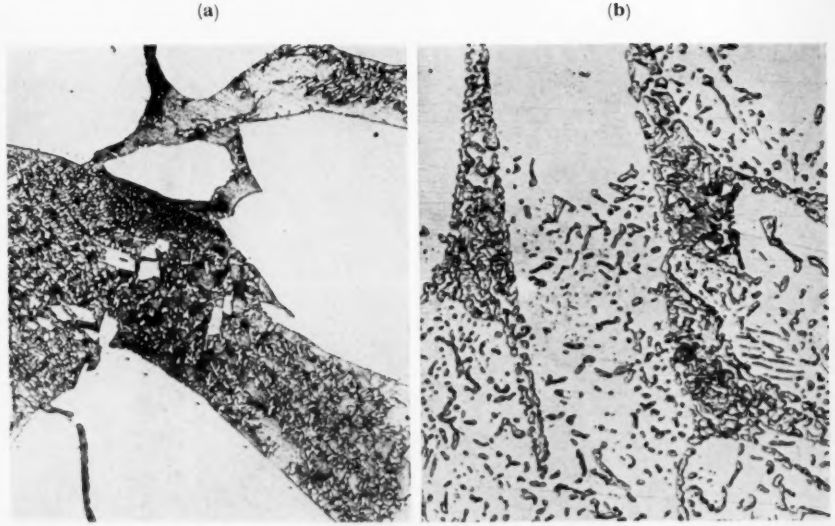

Fig. 3—Alloy **12*F*20** : annealed at 550° C. for 574 days, showing $\gamma + (\alpha \rightarrow \sigma)$ × 500

[*Cook and Brown*
[*To face p.* 348

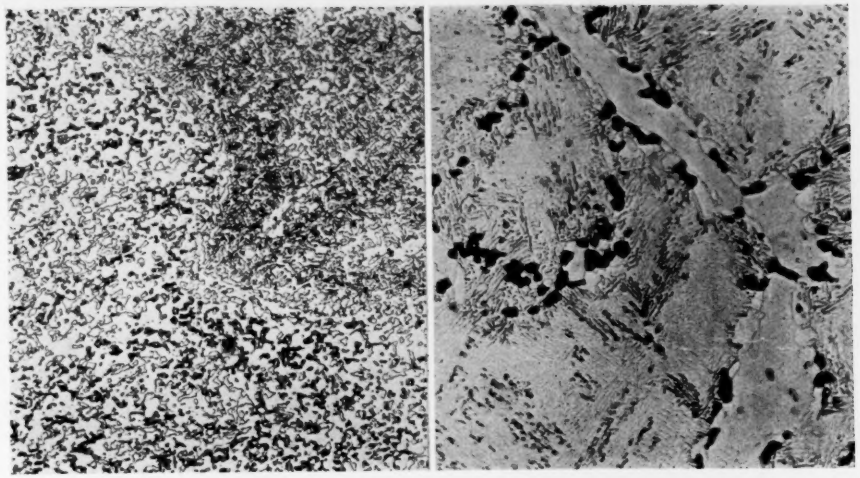

Fig. 4—Alloy 8*F*18 : cold-rolled, annealed at 550° C. for (*a*) 84 days, (*b*) 66 days, showing $\gamma + \alpha + \sigma$ × 500

Fig. 5—Alloy 12*F*19 : annealed at 550° C. for 535 days, showing $\gamma + \sigma$ ×500

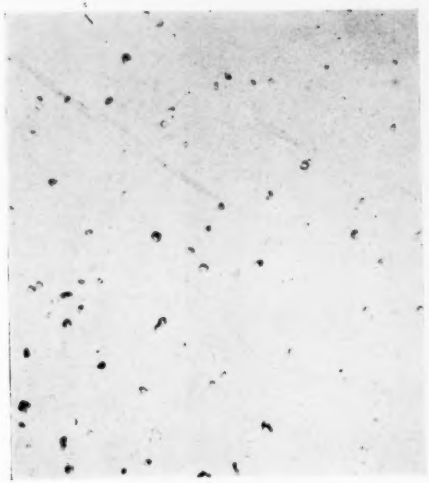

Fig. 6—Alloy 13*F*18 : cold-rolled, annealed at 550° C. for 84 days, showing $\gamma + \sigma$ × 500

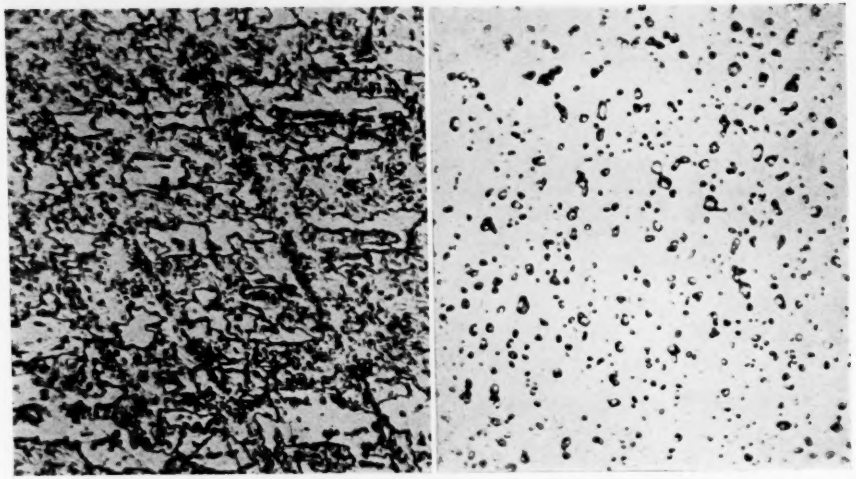

Fig. 7—Alloy 35*F*22 : cold-rolled, annealed at 550° C. for (*a*) 84 days, (*b*) 570 days, showing $\gamma + \alpha$ (*a*) × 500 (*b*) × 1500

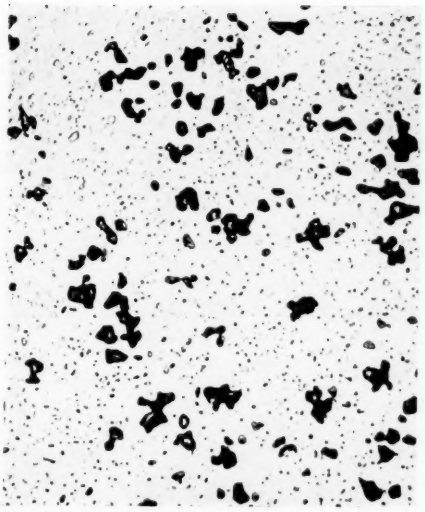

Fig. 8—Alloy 26*F*27 : cold-rolled, annealed at 650° C. for 176 days. Structure $\gamma + \alpha^1 + \sigma$ (etched dark). Etched in hot alkaline ferricyanide solution ×500

Fig. 9—Alloy 26*F*31 : cold-rolled, annealed at 650° C. for 44 days. Structure $\gamma + \alpha^1$ and trace of σ (etched dark). Etched in hot alkaline ferricyanide solution × 750

(a) (b)

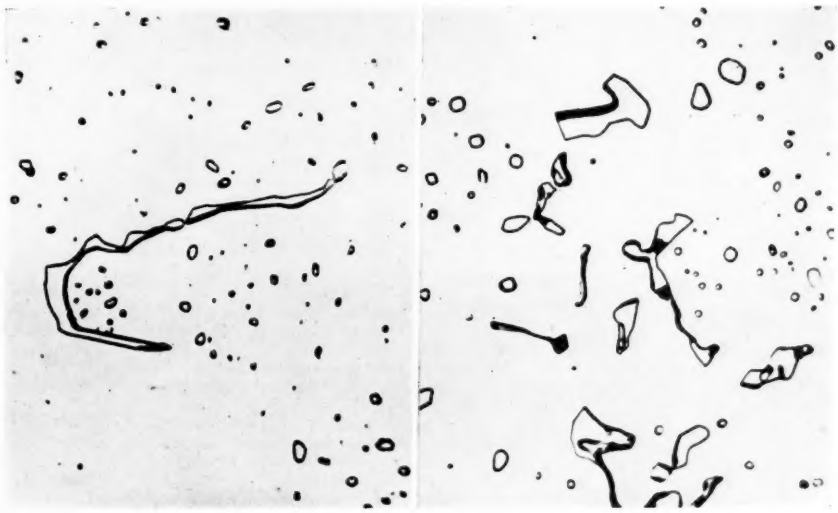

Fig. 10—Alloys cold-rolled and annealed at 800° C. for 200 days. Rounded particles are α^1, the irregular particles probably $Cr_{23}C_6$. Etched in hot alkaline ferricyanide solution.
(*a*) 35*F*25 ; (*b*) 37*F*29 × 1500

(*see* Table VI). Similarly, the presence of a small amount of a second phase in a microstructure was considered to be definite evidence of the alloy being duplex, even if the absence of a second constituent was indicated by the X-ray examination.

Constitutional Diagram at 550° C.

The diagram shown in Fig. 11 has been drawn from an assessment of the results of X-ray and microscopic examination of the annealed samples. The very small amounts of σ formed in the strain-free samples and the marked diffuseness of the X-ray diffraction lines of many of the alloys pointed to the probability that even after very long times of annealing, equilibrium at 550° C. may not have been attained. The phase boundaries shown in the diagram as dotted lines must be considered approximate. The only boundaries which it is thought can be fixed with any reasonable degree of accuracy are the $(\alpha + \sigma)/(\alpha + \gamma + \sigma)$ and the $\gamma/(\gamma + \sigma)$ boundaries.

The $(\alpha + \sigma)/(\alpha + \gamma + \sigma)$ boundary is fixed below 30% of Cr by 2*F*20, 2*F*25, 3*F*18, and 3*F*20, the first two being in the $(\alpha + \sigma)$ and the second two in the ternary $(\alpha + \gamma + \sigma)$ field. Lack of knowledge of the extent of the single-phase σ field prevents the σ triple point of the ternary field being fixed; this in turn causes some difficulty in deciding the exact position of the $(\gamma + \sigma)/(\alpha + \gamma + \sigma)$ boundary, since it is possible that the three alloys 5*F*30, 5*F*38, and 6*F*30, judged by their X-ray spectra, were not in equilibrium. The boundary drawn as a dotted line in Fig. 11 is in agreement with 9*F*20 in the ternary and 12*F*20 in the binary $(\gamma + \sigma)$ field. Its intersection

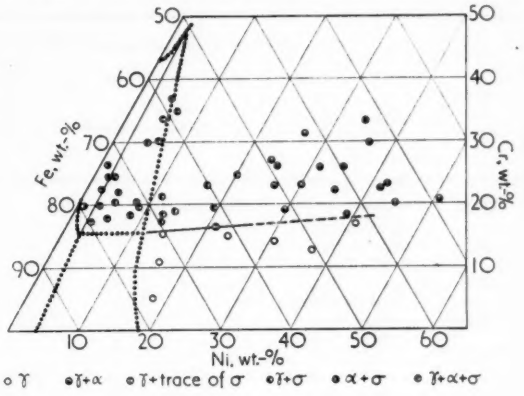

Fig. 11—Constitution diagram derived for 550° C.

Table IV

ALLOYS TREATED AT 550° C. AND EXAMINED AT THE UNITED STEEL COMPANIES' CENTRAL RESEARCH LABORATORIES

Alloy	Condition before Treatment	Microscopic Examination of Lump Samples		X-Ray Examination of Metal Powder Samples*			
		Microstructure and Probable Constitution	Time, days	Phases Identified	Time, days	Lattice Parameter of Phases, kX	
						γ	α'
12*F*19	γ strain-free	Traces of an intercrystalline constituent, $\gamma + \sigma$	535	$\gamma + \sigma$ (10–20%)	596	3·5782	
13*F*18	γ cold-worked	Precipitation of fine particles—probably $\gamma + \sigma$	84	$\gamma + \sigma$ (5%)	700	3·5780	
14*F*15	γ cold-worked	No change, γ	84	γ	700	3·5768	
14*F*20	γ strain-free	Traces of an intercrystalline precipitate, $\gamma + \sigma$?	535	$\gamma + \sigma$ (10–20%)	596	3·5778	
17*F*23	γ	Lump samples not examined		$\gamma + \sigma$ (10–20%)	700	3·5780	
19*F*20	γ			$\gamma + \sigma$ probably 25–35% σ	700	3·5775	
21*F*17	γ cold-worked	Traces of precipitate, $\gamma + \sigma$?	84	γ	700	3·5765	
30*F*19	γ cold-worked	General fine precipitation	84	$\gamma + \alpha$	596	3·5762	
32*F*14	γ strain-free	Slight precipitation, $\gamma + \sigma$?	535	γ	596	3·5750	
33*F*33	γ strain-free	Some intercrystalline constituent and precipitation in body of crystals, $\gamma + \alpha$	528	$\gamma + \alpha$ (20%)	626	3·5740	2·8747
38*F*18	γ strain-free	Very slight traces of precipitation, $\gamma + \alpha$	528	$\gamma + \alpha$ (trace)	596	3·5740	
38*F*18	γ cold-worked	More evidence of precipitation, $\gamma + \alpha$	84				
41*F*24	γ cold-worked	Recrystallization incomplete. Some signs of precipitation, $\gamma + \alpha$	84	Not treated			
48*F*22	γ cold-worked	Fine-grained structure containing some coarse precipitate, $\gamma + \alpha$	84	Not treated			
35*F*22	γ cold-worked	Recrystallization incomplete. Some signs of precipitation, $\gamma + \alpha$	84	$\gamma + \alpha$ (10%)	626	3·5748	2·8734
42*F*23	γ strain-free	Small quantity of an intercrystalline constituent, $\gamma + \alpha$	528	$\gamma + \alpha$ (10–15%)	510	3·5722	2·8745
45*F*19	γ strain-free	Similar to 42*F*23, $\gamma + \alpha$	528	$\gamma + \alpha$ (trace)	596	3·5715	2·8735

* Metal powders annealed in cold-worked condition

Table V

ALLOYS TREATED AT 550° C. AND EXAMINED AT THE NATIONAL PHYSICAL LABORATORY

Alloy	Microscopic Examination of Lump Samples			X-Ray Examination of Metal Powder Samples*			
	Condition before Treatment	Structure and Probable Constitution	Time, days	Phases Identified	Time, days	Lattice Parameter of γ-Phase, kX	Magnetic Observations†
1F20	α strain-free	Unchanged α	415	α + σ	710		S
	cold-worked	,, α	66				
1F25	α strain-free	,, α	590	α + σ	710		S
	cold-worked	,, α	66				
1F30	α strain-free	,, α	590				
	cold-worked	,, α	66				
2F20	α strain-free	,, α	590	α + σ	710		S
	cold-worked	,, α	66				
2F25	α strain-free	,, α	415	α + σ	710		S
	cold-worked	Small amount of γ formed α + γ	66				
3F25	α strain-free	Unchanged α	590	α + σ + γ	710		S
	cold-worked	Small amount of γ formed α + γ	66				
5F18	γ+α strain-free	Small amount of σ (α + α₂ + σ)	590	α + γ + σ	710		S
3F18	α cold-worked	Small quantities of γ with possible traces of σ at interfaces of γ and α	66				
3F20	α cold-worked		66	α + γ + σ ?			
5F20	α+γ cold-worked		66				
5F34	α strain-free	Dense striated precipitate σ + α	415	α + σ + γ	710		MS
5F38	α strain-free	,, ,, ,, σ + α	160	α + γ + σ	160		S
6F30	α	Not examined		α + γ + σ	320		MS
6F35	α strain-free	Very dense fine precipitate	60	σ + γ	57		MS
8F18	γ+α strain-free	Small amount of σ (γ + α + σ)	415	γ + α + σ	710		W
	cold-worked	,, ,, ,, ,, (γ + α + σ)	66				
8F20	γ+α strain-free	Some σ around α zones	415	γ + α + σ	710		S
	cold-worked	Traces of σ. Ferrite decomposing	66				
9F20	γ+α strain-free	Small amount of σ (γ + α + σ)	415	γ + α + σ	710		S
	cold-worked	,, ,, ,, ,,	66				
12F19	γ cold-worked	General precipitation γ + σ	154				
12F20	γ + α strain-free	No σ visible. Ferrite decomposing (γ + α)	415	γ + σ	710	3·5780	VW
13F18	γ strain-free	No change γ	570				
	cold-worked	Small particles precipitated γ + σ ?	154				
14F15	γ strain-free	No change γ	570				
	cold-worked	Traces of precipitation γ + σ ?	154				
16F11	γ strain-free	No change γ	160	γ + α₂	169	3·5745	W
17F23	γ strain-free	No change γ	160				W
18F5	α₂ strain-free	Mainly distorted α	60	γ + α₂	57	3·5736	S
21F17	γ strain-free	No change γ	160				
	cold-worked	Possible traces of precipitate γ + σ ?	154				
23F14	γ strain-free	Unchanged γ	60	γ	57	3·5757	VW
23F25	γ	Not examined		γ + α	700	3·5765	VW
26F24	γ strain-free	No change γ	160	γ + α	700	3·5770	W
26F26	γ strain-free	Traces of precipitate in boundaries γ + α ?	160	γ + α	700	3·5770	VW
30F19	γ cold-worked	Small quantity of clear etching particles γ + α	154				
35F12	γ strain-free	Unchanged γ	60	γ	57	3·5757	S
35F22	γ cold-worked	General precipitation of clear etching particles γ + α	570	γ + α	590	3·5745	W
38F18	γ cold-worked	Uncertain traces of fine precipitate γ + α ?	154				
41F16	γ strain-free	Unchanged γ	574	γ	590	3·5741	MS
48F22	γ	Not examined		γ	57	3·5696	W

* Metal powders annealed in cold-worked condition
† Response to magnet: S = strong M = medium W = weak

with the $\gamma/(\gamma+\sigma)$ boundary fixed the γ triple point at 11·5% of Ni and 15·5% of Cr. The position of the $(\alpha+\gamma)/(\alpha+\gamma+\sigma)$ boundary has not been fixed with great accuracy as there were no alloys containing between 2 and 12% of Ni and less than 18% of Cr available for examination. The proportion of σ found in 2*F*20, 3*F*18, and 5*F*18 afforded the evidence for placing this boundary in the position as drawn.

The $\gamma/(\gamma+\sigma)$ boundary is believed to be fairly accurately fixed below 20% of Ni. With the exception of alloy 30*F*19, in which there was some evidence of both α and σ in the heat-treated cold-worked lump sample, none of the alloys examined was found to be in the $(\gamma+\sigma+\alpha')$ ternary field at 550° C., so the extent to which the $\gamma/(\gamma+\sigma)$ boundary extends across the diagram is uncertain. All the alloys containing more than 21% of Ni and 18% of Cr precipitated an α-phase at 550° C., but it is not certain at what composition this phase can be considered as being an equilibrium phase.

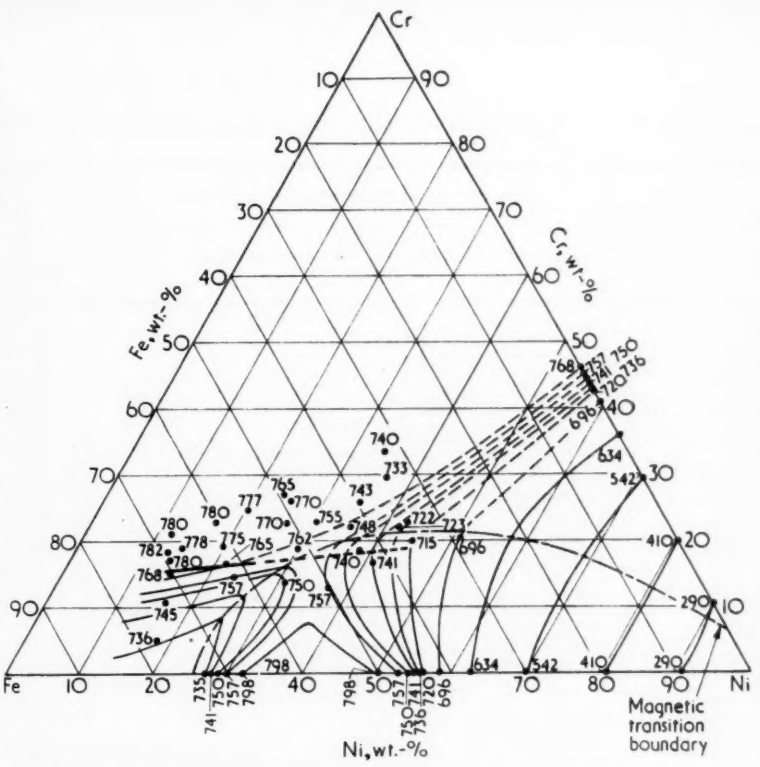

Fig. 12—Lattice parameter values of γ-phase in alloys annealed at 550° C.

An estimation of the position of the $\gamma/(\gamma+\sigma)$ boundary was also made from the lattice-parameter values of the γ-phase. The iso-parameter contours for the gamma field have been previously established[5] and these, together with the lattice parameter values at 550° C., are plotted in Fig. 12. For alloys in which precipitation of a second phase has taken place the parameter values fall below those indicated by the iso-parameter contours. For such alloys the parameter values for the γ-phase are lower than were found after annealing at 650° C. The position of the γ-phase boundary deduced from the lattice parameter values agrees with that given in Fig. 11.

CONSTITUTION AT 650° AND 800° C.

In iron-rich alloys the σ comes to equilibrium with austenite, whereas in nickel-rich alloys the phase that comes to equilibrium with austenite is the body-centred phase based on chromium, known usually as α'. In some intermediate range a ternary field comprising γ, σ, and α' is to be expected. This field was not defined in the paper by Rees, Burns, and Cook, although the evidence suggested that it occurred at about 33% of Ni. Difficulties arose from the fact that the formation of a precipitate of α' is not necessarily evidence that the alloy lies in the $(\gamma+\alpha')$ or $(\gamma+\alpha'+\sigma)$ field, for the α' may subsequently transform to σ, and long annealings are necessary to ensure that equilibrium has been achieved. Furthermore, there were discrepancies between the results of microscopic and X-ray examination which could not be explained. A number of additional experiments have been made, and have removed some of the contradictions.

Constitution at 650° C.

According to the previous work, there was only one alloy near the γ field boundary having the constitution $(\gamma+\alpha'+\sigma)$. This contained 26·4% of Ni and 31·2% of Cr (26*F*31), and the amount of σ was such that it was not detected by X-rays. Two more alloys were therefore made up, one slightly poorer in nickel and the other slightly richer. The actual analyses were 26·1% of Ni/27·08% of Cr (26*F*27), and 29·6% of Ni/30·2% of Cr (30*F*31). The 26% Ni alloy after 176 days' annealing at 650° C. with intermittent cold-rollings showed an undoubted $(\gamma+\alpha'+\sigma)$ structure (Fig. 8), and this was confirmed by X-ray examination of powder filed from the annealed strip. The other showed no trace of sigma. The amount of σ found in the 26·4% Ni–31·2% Cr alloy was very small (Fig. 9), and it is therefore likely that the boundary between the $(\gamma+\alpha')$ and the $(\gamma+\alpha'+\sigma)$ fields runs very close to the composition of this alloy. The boundary between the $(\gamma+\sigma)$ and $(\gamma+\alpha'+\sigma)$ fields must lie on the low nickel side of alloy 26*F*27, since a less drastic annealing caused the α' phase to disappear

Table VI

SUMMARY OF MICROSCOPIC AND X-RAY EXAMINATION OF ALLOYS ANNEALED AT 550° C.

Alloy	Microscopic Examination of Lump Samples			X-Ray Examination of Metal-Powder Samples*		
	Quenched from High Temp.	Details of Treatment and Microstructure of Alloys after Annealing	Time of Anneal, days	Phases Identified	Time of Anneal, days	Lattice Parameter of γ, kX
1F20	α	strain-free; unchanged α	415	$\alpha + \sigma$	710	
		cold-worked; unchanged α	66			
1F25	α	strain-free; unchanged α	590	$\alpha + \sigma$	710	
		cold-worked; unchanged α	66			
1F30	α	strain-free; unchanged α	590	Not examined		
		cold-worked; unchanged α	66			
2F20	α	strain-free; unchanged α	590	$\alpha + \sigma$	710	
		cold-worked; α and possibly some σ	84			
2F25	α	strain-free; unchanged α	415	$\alpha + \sigma$	710	
		cold-worked; α and traces of unidentified constituent	84			
3F18	α	cold-worked; α, γ, and possibly some σ	66	$\alpha + \sigma + \gamma$	590	
3F20	α	cold-worked; α, γ, and possibly some σ	66	$\alpha + \sigma + \gamma$	590	
3F25	α	strain-free; unchanged α	590	$\alpha + \gamma + \sigma$	710	
		cold-worked; α and a small amount of γ	66			
5F18	$\alpha + \gamma$	strain-free; α, α_2, and a small amount of σ	590	$\alpha + \gamma + \sigma$	710	
5F20	$\alpha + \gamma$	cold-worked; α, γ, and a trace of σ	66	$\alpha + \gamma + \sigma$	590	
5F22	α	strain-free; α and γ	524	$\alpha + \gamma + \sigma$	590	
5F30	α	cold-worked; α, γ, and indications of σ along crystallographic planes	84	Not examined		
5F34	α	strain-free; α and a dense striated precipitate—probably much σ	415	$\alpha + \gamma + \sigma$	710	
5F38	α	strain-free; α and a dense striated precipitate—probably much σ	160	$\alpha + \gamma + \sigma$	160	
6F30	α	cold-worked; α, γ, and indications of σ along crystallographic planes	84	$\alpha + \gamma + \sigma$	320	
6F35	α	strain-free; α and a dense fine precipitate—probably σ	60	$\sigma + \gamma$	57	
8F18	$\gamma + \alpha$	strain-free; γ, α, and a small amount of σ	415	$\gamma + \alpha + \sigma$	710	
		cold-worked; decomposition in the two phases, probably σ formed	84			
8F20	$\gamma + \alpha$	strain-free; γ, α, and a small amount of σ	415	$\gamma + \alpha + \sigma$	710	
		cold-worked; γ, α, and traces of σ	66			
9F20	$\gamma + \alpha$	strain-free; γ, α, and a small amount of σ	415	$\gamma + \alpha + \sigma$	710	
		cold-worked; γ, α, and traces of σ	66			
12F19	γ	strain-free; γ and possibly traces of σ in the grain boundaries	535	$\gamma + \sigma$	596	3·5782
		cold-worked; γ and general precipitate—possibly σ	154			
12F20	$\gamma + \alpha$	strain-free; α decomposed, and localized precipitation in γ, identity uncertain	574	$\gamma + \sigma$	710	3·5780
13F18	γ	strain-free; unchanged γ	570	$\gamma + \sigma$	700	3·5780
		cold-worked; γ and general precipitate in grains	154			
14F15	γ	strain-free; unchanged γ	570	γ	700	3·5768
		cold-worked; γ and possible traces of precipitate	154			
14F20	γ	strain-free; γ and traces of intercrystalline precipitate	535	$\gamma + \sigma$	596	3·5778
16F11	γ	strain-free; unchanged γ	160	$\gamma + \alpha_2$	169	3·5745
17F23	γ	strain-free; γ and traces of intercrystalline precipitate, probably σ	574	$\gamma + \sigma$	700	3·5780
18F5	α_2	strain-free; Widmanstatten structure	60	$\gamma + \alpha_2$	57	3·5736
19F20	γ	strain-free; γ and traces of intercrystalline precipitate	574	$\gamma + \sigma$	700	3·5775
		cold-worked; γ and precipitated particles of σ	84			
20F25	γ	not examined		γ + trace of σ	596	3·5777
21F17	γ	cold-worked; γ and traces of precipitated particles of σ	154	γ	700	3·5765
23F14	γ	strain-free; unchanged γ	60	γ	57	3·5757
23F25	γ	strain-free; γ and traces of intercrystalline precipitate, identity uncertain	570	$\gamma + \alpha$	700	3·5765
26F24	γ	strain-free; γ and traces of intercrystalline precipitate	574	$\gamma + \alpha$	700	3·5770
		cold-worked; γ and general precipitation in grains	574			
26F26	γ	strain-free; γ and traces of intercrystalline precipitate, identity uncertain	574	$\gamma + \alpha$	700	3·5770
30F19	γ	cold-worked; γ and a small amount of clear etching precipitate, probably α	154	$\gamma + \alpha$	596	3·5762
30F23	γ	cold-worked; γ and some precipitation along crystallographic planes; recrystallization incomplete	218	γ + trace of α	218	3·5755
31F26	γ	strain-free; γ and traces of intercrystalline precipitate, probably α	570	Not examined		
32F14	γ	strain-free; unchanged γ	535	γ	596	3·5750
33F33	γ	strain-free; γ and intercrystalline precipitate, also precipitation in grains	528	$\gamma + \alpha$	626	3·5740
35F12	γ	strain-free; unchanged γ	60	γ	57	3·5757
35F22	γ	strain-free; γ and intercrystalline precipitate	570	$\gamma + \alpha$	590	3·5748
		cold-worked; γ and general precipitate of fine particles, probably α	570			
35F25	γ	cold-worked; γ and some precipitation along crystallographic planes. Recrystallization incomplete	218	$\gamma + \alpha$	218	3·5743
37F29	γ	cold-worked; γ and some precipitation along crystallographic planes. Recrystallization incomplete	218	$\gamma + \alpha$	218	3·5733
38F18	γ	strain-free; γ and traces of precipitation	528	$\gamma + \alpha$	596	3·5740
		cold-worked; γ and doubtful traces of precipitation	154			
41F16	γ	strain-free; unchanged γ	574	γ	590	3·5741
41F24	γ	cold-worked; γ and some precipitation along crystallographic planes. Recrystallization incomplete	84	γ + trace of α	450	3·5723
42F23	γ	strain-free; γ and traces of an intercrystalline constituent, probably α	528	$\gamma + \alpha$	510	3·5722
45F19	γ	strain-free; γ and traces of an intercrystalline constituent, probably α	528	$\gamma + \alpha$	596	3·5715
48F22	γ	cold-worked; γ and a small amount of general precipitate, probably α	84	γ	57	3·5696

* Metal powders annealed in cold-worked condition

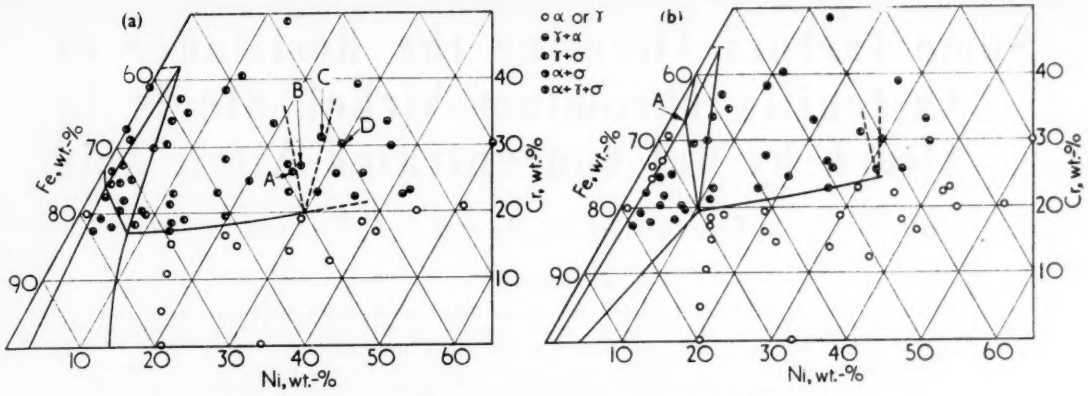

Fig. 13—Constitution diagram derived for (*a*) 650° C., (*b*) 800° C.

from an alloy with 25% of Ni and 26% of Cr (26*F*26); the boundary probably runs between these two compositions. The suggested position of the ternary field is given in Fig. 13*a* and the positions of the four alloys discussed are indicated at *A* (26*F*26), *B* (26*F*27), *C* (26*F*31), and *D* (30*F*31).

Constitution at 800° C.

The position of the $(\gamma + \alpha' + \sigma)$ field had been uncertain because two alloys in the region of composition 25–30% of Cr and 35–40% of Ni were reported in the X-ray examination to consist of $(\gamma + \alpha')$ and by the microscopic examination to consist of $(\gamma + \alpha' + \sigma)$. Photographs of these alloys, etched in alkaline ferricyanide, are reproduced in Figs. 10*a* and *b*; the large irregular particles were thought to be sigma. The precipitates were extracted from these alloys by the method described by Kirkby and Morley[4] (electrolytic extraction in a solution of potassium iodide, citric acid, and hydrochloric acid), and on X-ray examination proved to consist of α' and $Cr_{23}C_6$. These samples had been periodically embedded in plastic for microscopic examination, and it is clear that in spite of the precautions that had been taken to clean the surfaces before re-annealing, carburization had occurred. These alloys are therefore assigned to the $(\gamma + \alpha')$ field. A new alloy containing 30% of Ni and 30% of Cr also proved to be in the $(\gamma + \alpha')$ field. Further annealings have been carried out on an alloy containing 31% of Ni and 26% of Cr; it had previously been uncertain whether this lay in the $(\gamma + \sigma)$ or the $(\gamma + \alpha' + \sigma)$ field. After seven rolling operations and annealings totalling 175 days, some carburization had occurred, but α' was shown to be present by X-ray examination of the strip, and there was a faint trace of sigma. It is likely therefore that this alloy lies, if not in, at least very near the $(\gamma + \alpha' + \sigma)$ field. According to the information now available, the $(\gamma + \alpha' + \sigma)$ field must be very narrow, and its probable position is indicated in Fig. 13*b*.

A further uncertainty was previously reported in the position of the α triple point of the $(\gamma + \alpha + \sigma)$ field at 800° C. (*A*, Fig. 13*b*). This arose in the interpretation of the structure of the alloy containing 1% of Ni and 30% of Cr. Traces of a constituent thought to be σ were found microscopically and could not be found by X-rays. This alloy had readily precipitated σ at 650° C., and fresh samples were annealed for periods of two months at 750° and 800° C. In neither case was σ produced, and it is therefore concluded that the α triple point of the $(\gamma + \alpha + \sigma)$ field lies above 30% of Cr about in the position given in Fig. 13*b*.

Acknowledgment

The work was carried out in the Metallurgy Division of the National Physical Laboratory as part of the general research programme of the Laboratory, and is published by permission of the Director of the Laboratory.

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Some Factors Affecting the Resistance of Austenitic Chromium–Nickel Steels to Attack by Hot Concentrated Nitric Acid

By H. T. Shirley, B.Sc., A.R.C.S., and J. E. Truman, A.Met.

SYNOPSIS

This paper is the second of three dealing with the behaviour of higher chromium–nickel steels in concentrated nitric acid. Certain factors which influence the resistance of normally heat-treated unwelded 18/13/1 Cr–Ni–Nb type steel to boiling 70% HNO_3 are discussed.

The presence of intercrystalline penetration appears to be characteristic under these conditions, even with steels effectively stabilized against ordinary carbide precipitation effects. Development of a shallow network of intercrystalline penetration is considered to contribute to initial increase in rate of attack with time, and large-grained structures can make this effect more serious. Purity of acid also influences the rate of attack. Small additions of several acid radicals were made, and of these hydrofluoric acid proved most damaging. A much greater effect, however, was produced by metallic contamination from dissolved steel, and the main influence is shown to be due to the chromium content of the solution. This factor (for appropriate relationships between time, volume of solution, and surface area of steel) can very greatly magnify the smaller increases from other causes. Combined with initial variability, which is attributed to variable passivity, it can explain the large differences in loss of weight that were found in successive test cycles. This effect of metallic contamination falls off rapidly with reduction in acid strength, and in practice is probably not serious below 60% HNO_3.

A STUDY of various structural and quantitative aspects of the attack by boiling 70% HNO_3 (sp. gr. 1·42) on a number of acid-resisting chromium–nickel steels has already been published.* This showed that the niobium-stabilized 18/13/1 and 18/9/1 type steels were free from deleterious effects associated with heat-treatment introduced by welding. In selecting material for plant to resist boiling 70% HNO_3, it was felt that the higher-nickel steel might be the safer choice because of its greater austenitic stability, in view of the accelerated interconstituent attack observed in some duplex materials.* The present paper deals primarily with tests covering various aspects of the attack on unwelded, normally heat-treated 18/13/1 material; considerable variability can occur in testing, and the significance of some of the responsible factors has been studied. Some tests on 18/9/1 Cr–Ni–Nb steel and on a plain 25/20 steel have been included for general comparison.

EXPERIMENTAL PROCEDURE

The analyses of the steels tested are given in Table I. Unless otherwise stated, the test samples were 3 in. × 1 in. specimens sheared from 10-gauge works-softened sheet (air-cooled from 1050° C.). The specimens were laboratory-treated after shearing, to remove the cold work associated with shearing, and were air-cooled from 1050° C., except for the 25/20 Cr–Ni steel 7, which was water-quenched from the same temperature. They were then pickled in a hydrochloric/nitric acid bath, and were tested individually in 250 ml. of solution in 500-ml. flasks fitted with open reflux condensers.

In some of the tests relating to the effects of metallic radicals and cold work, supply considerations made scaling-down essential. No strict quantitative comparison was made between this series and others, but the relationship between rate of attack and accumulation of dissolved metal was maintained constant by keeping the ratio between surface area of specimens and volume of acid at a constant value.

INFLUENCE OF DEGREE OF IMMERSION

Preliminary tests were carried out with steel 1,

* H. T. Shirley and C. G. Nicholson, *J. Iron Steel Inst.*, 1952, vol. 170, pp. 111–118.

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Table I

ANALYSES OF STEELS TESTED

Steel		C, %	Si, %	Mn, %	Cr, %	Ni, %	Nb, %	Cu, %	Mo, %	W, %	N, %
18/13/1 Cr–Ni–Nb	1	0·11	0·70	1·30	17·96	13·40	1·48	0·07	0·05	0·07	0·043
	2	0·12	0·74	1·42	18·26	14·03	1·39	0·06	0·10	0·05	0·045
	3	0·10	0·77	1·18	18·72	13·35	1·36	0·12	0·26	0·05	0·045
	4	0·05	0·45	1·39	18·85	13·06	0·93	0·13	0·06	0·02	0·069
	5	0·08	0·72	1·08	18·24	13·58	0·57	0·06	0·03	Nil	0·046
18/9/1 Cr–Ni–Nb	6	0·13	0·67	0·48	18·32	9·13	1·32	...	...	...	0·044
25/20 Cr–Ni	7	0·11	1·58	0·77	24·74	21·20	Nil	...	...	...	0·070

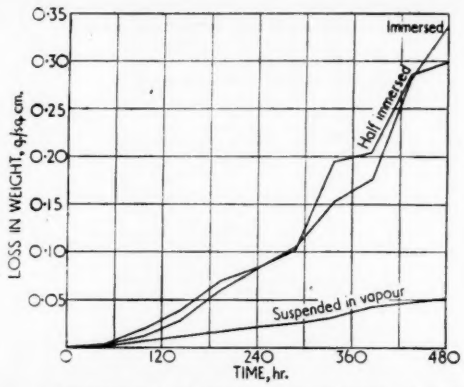


Fig. 1—Comparison of tests on specimens of steel 1 immersed, partially immersed, and in condensing vapour of boiling 70% HNO_3

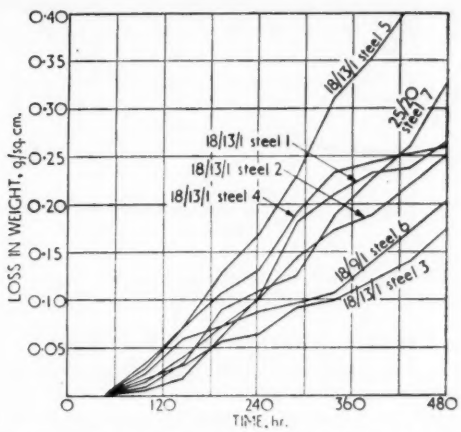


Fig. 2—Attack after immersion for 480 hr. in boiling 70% HNO_3 (A.R.)

using boiling 70% HNO_3, by comparing specimens immersed, half-immersed, and suspended in the vapour with condensate dripping on to the specimen. The acid, which was of laboratory reagent quality, was renewed at 6, 24, and 48 hr., and thereafter at 48-hr. intervals to 480 hr. The losses in weight of the samples at each renewal are plotted in Fig. 1. The solution products from the steel have a cumulative accelerating action on attack (*see* pp. 356–358), and this is probably largely responsible for the considerably lower rate of attack in the vapour and condensate; complete or partial immersion gave very similar results, and all subsequent tests were made with the specimens immersed.

COMPARISON OF MATERIALS

Losses in weight after immersion for 480 hr. in boiling 70% HNO_3 are plotted in Fig. 2. Of the five casts of 18/13/1 material, steels 1, 2, and 3 were from one works and steels 4 and 5 were each from different works. The attack on steel 5 was the worst, and a structural reason for this is discussed in the next paragraph. The 25/20 Cr–Ni steel 7, also, was inferior to the others. The remainder showed some variability from cycle to cycle, but from the point of view of average resistance they can be regarded as a group.

Micro-examination of sections from these samples confirmed earlier observations* that there is a general tendency for slight intercrystalline penetration of these steels in boiling 70% HNO_3, independent of heat-treatment in the 500–800° C. range. This tendency occurred in samples of niobium-stabilized material, water-quenched from 1050° C., and in the 18/13/1 material the penetration was not increased by the 650° C. treatment induced during welding. The effect normally penetrates to a depth of only one or two crystals below the surface at any given time, but it is evidently capable of appreciably increasing the real and apparent rates of attack, by effectively increasing the exposed surface and possibly also by direct detachment of grains. The extent of the effect is illustrated in Fig. 5, which shows surface and sectional views of steel 1. The accelerating rate of attack, which is common to the early cycles, probably relates primarily to the initial development of this network penetration. The attack on steel 5 (*see* Fig. 6) is particularly interesting in this respect. By some unusual combination of production factors, the sheet representing this cast had a mixed grain-size showing a series of large 'plate-like' crystals embedded in a much finer grained matrix. Much less grain-boundary attack is required to detach the large grains, compared with a similar volume of finer-grained material. This, presumably, is the primary reason for the greater loss in weight from steel 5. This initial increase in rate of attack is liable to be greatly magnified by the cumulative acceleration produced by the presence of dissolved metal in the acid (*see*

* Shirley and Nicholson, *loc. cit.*

Table II

RATES OF ATTACK IN SUCCESSIVE TEST PERIODS

Steel	Heat-Treatment	Loss in Weight, g./sq. cm., in 24 hr., After Period:						
		0–6 hr.	6–24 hr.	24–48 hr.	48–96 hr.	96–144 hr.	144–192 hr.	192–240 hr.
1	1050° C., Air-cooled	0·0006	0·0005	0·0005	0·0026	0·0057	0·0227	0·0198
2	1050° C., Air-cooled	0·0007	0·0005	0·0015	0·0106	0·0180	0·0119	0·0144
3	1050° C., Air-cooled	0·0006	0·0004	0·0008	0·0084	0·0071	0·0118	0·0037
4	1050° C., Air-cooled	0·0005	0·0004	0·0018	0·0158	0·0188	0·0148	0·0109
5	1050° C., Air-cooled	0·0006	0·0006	0·0016	0·0135	0·0221	0·0292	0·0167
6	1050° C., Air-cooled	0·0007	0·0006	0·0014	0·0076	0·0109	0·0150	0·0081
7	1050° C., Water-quenched	0·0010	0·0007	0·0009	0·0046	0·0117	0·0276	0·0091

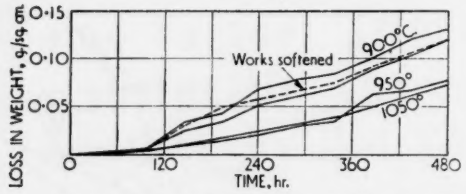


Fig. 3—Effect of cold-working followed by annealing (steel 1)

pp. 357–358), which accounts for the very large losses suffered in some of the later cycles (*see* Table II).

TEST RELATING TO COLD WORK

It was thought that some improvement might be effected by moderate cold-working of the specimens, followed by annealing at 900° C., as a result of the formation of new crystal boundaries, and possible grain refinement. A piece of the 10-gauge sheet from steel 1 was therefore cold-rolled to 20% reduction, and samples were treated for 30 min. at 900° C., 15 min. at 950° C., 10 min. at 1000° C., or 7 min. at 1050° C. These samples were then tested for 480 hr. To ensure comparable acid conditions, a sample of the original works-softened (1050° C.) sheet was included. Each cycle was carried out in acid from a single Winchester, drawn from one delivery of laboratory-reagent-quality acid, up to 384 hr. of test, and from a second delivery of acid for the remainder of the test. The losses are plotted in Fig. 3, and there is the usual variability between cycles. Figure 7 is a section through the surface of the 900° C. annealed sample, after test (*cf.* Fig. 5*b*, showing the works-softened material before cold rolling). Despite the appreciable distortion and breakdown of grain structure resulting from the treatments, there was no consistent improvement in acid resistance.

EFFECT OF CHANGES IN SUPPLY AND QUALITY OF ACID

The final losses in this cold-worked series were only about half those for this steel in the earlier 480-hr. series (Fig. 2). The acid used in the earlier test was a previous delivery from the same source, but it seemed possible that small amounts of impurities might have significant effects. Accordingly, it was decided to compare three supplies of acid. Two were of the same grade and from the same source as those already used for the tests, *i.e.*, synthetic nitric acid

Table III

EFFECT OF ADDITION OF ACID RADICALS ON RESISTANCE OF 18/13/1 Cr–Ni–Nb STEEL 1

Acid Addition, 1 c.c./litre	Loss in Weight, g./sq. cm., After:	
	6 hr.	24 hr.
None	0·0003	0·0013
HNO_2	0·0003	0·0013
HCl	0·0002	0·0011
H_2SO_4	0·0005	0·0022
H_3PO_4	0·0008	0·0030
HF	0·0047	0·0081

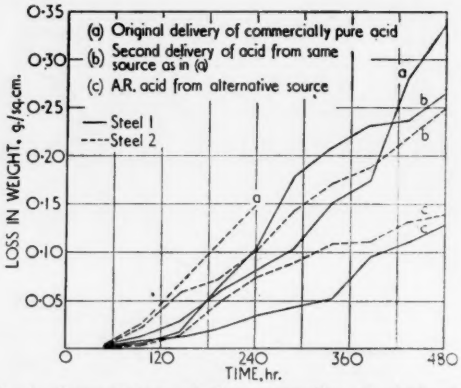


Fig. 4—Comparison of three supplies of nitric acid

distilled in silica and collected in chemical stoneware. The chloride and sulphate contents were less than 0·0005%. The third supply was A.R. acid from another source, prepared to the specification :

	% max.		% max.
Cl	0·0001	Heavy metals and Fe	0·0001
IO_3	0·0005	As_2O_3	0·0001
SO_4	0·0002	Residue	0·005

The results of the 480-hr. tests are plotted in Fig 4 ; the general level of attack in the first two solutions is similar and of the same order as in the tests shown in Figs. 1 and 2. The average losses in the A.R. acid were only about half as great, giving totals of the order of those in Fig. 3.

INFLUENCE OF ADDED 'IMPURITIES'

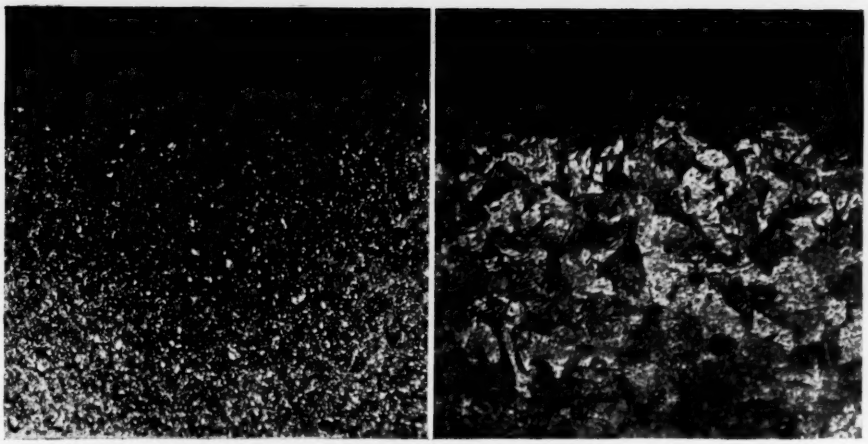
Effect of Acid Radicals

Tests were made to determine the extent to which relatively large additions of acid radicals would affect the attack, because some contamination of this type might occur in service. Additions of 0·1% (by volume) of various concentrated acids were made to the original supply of 70% HNO_3. The tests were made with samples of steel 1 in 200 ml. of solution for 6 and 24 hr. at boiling point, the acid being changed at the 6-hr. stage. The results, given in Table III, show that hydrofluoric acid had the most serious effect, the attack increasing very markedly in the first 6 hr. and after 24 hr. being about six times greater. When this test was continued for a further 24 hr., the average loss in weight was found to be 0·0070 g./sq. cm., compared with 0·0015 g./sq. cm. when there was no addition of acid. The effect of the hydrofluoric acid was not related to any obvious increase in intensity of intercrystalline penetration, and even in this test the rate of attack remained well below that ultimately achieved in the 48-hr. cycles of the 480-hr. tests in plain acid (*see* Table II).

Effect of Addition of Metallic Ions

To study the effect of accumulating metallic ions, pickled and emeried samples of steel 1 were tested for 24 hr. in 250 ml. of 70% HNO_3, followed by a second test in fresh acid, two further 24-hr. cycles in the same acid, and finally a fifth 24-hr. cycle using fresh acid. Losses in weight, g./sq. cm., over these periods were as follows :

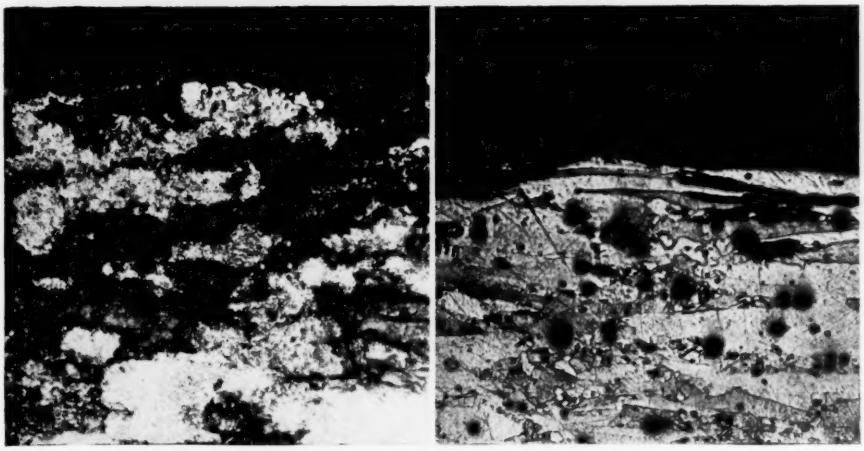
(a)



(b)

Fig. 5—Steel 1 after test in boiling 70% HNO_3 : (*a*) Surface appearance × 50 ; (*b*) etched section through surface of sample in (*a*) × 500

(a)



(b)

Fig. 6—Steel 5 after test in boiling 70% HNO_3 : (*a*) Surface appearance × 50 ; (*b*) etched section through surface of sample in (*a*) × 200

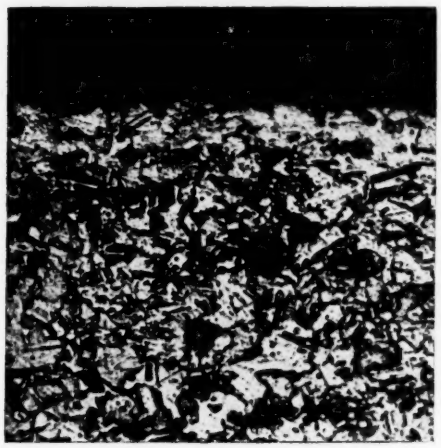


Fig. 7—Etched section of steel 1 after 20% reduction by cold-rolling, 20 min. treatment at 900° C., and testing in boiling 70% HNO_3 × 500

Test	Pickled Sample	Emerled Sample
1st	0·0016	0·0017
2nd (Fresh acid)	0·0025	0·0012
3rd (Acid from 2nd)	0·0381	0·0178
4th (Acid from 3rd)	0·1118	0·0875
5th (Fresh acid)	0·0045	0·0109

Although the heavy attack in the 3rd and 4th cycles appears to have made the samples liable to higher attack in the fresh acid of the 5th cycle, the increase is much less than that induced by contamination of the acid in the 3rd and 4th cycles.

The effect of metallic contamination was studied in more detail by adding varying amounts of ' used ' acid to fresh acid. (The ' used ' acid additions were from 250 ml. of 70% HNO_3, in which a 3 in. × 1 in. sample of steel 1 had been tested for 72 hr., successive 24-hr. losses being 0·0104, 0·1283, and 0·1377 g./sq. cm.) The tests were carried out on 3 in. × 1 in. samples of steel 3 exposed for 24 hr. in 250 ml. of the solutions at boiling point. The results (Table IV) show that the maximum attack, about 0·1 g./sq. cm., occurred in solution which initially contained dissolved steel in an amount corresponding to a prior attack of 0·01 g./sq. cm. on a 3 in. × 1 in. sample of steel 1 in 250 ml. of acid.

Various additions were also made of pure nickel, chromium nitrate, or iron nitrate,* and the results are given in Table IV. Nickel has no appreciable influence and iron has a possible but erratic effect, but chromium has a very marked action, and is obviously the major cause of the accelerated attack resulting from the addition of dissolved steel. However, the effect of chromium is not so severe as that due to the equivalent amount of dissolved steel, and probably there are other more complex effects occurring in the latter case.

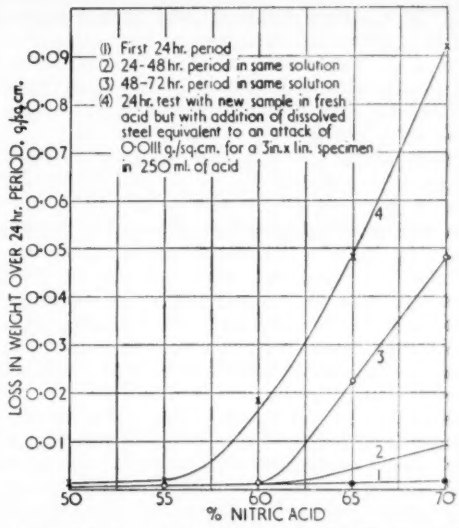


Fig. 8—Tests on 18/13/1 steel 3, showing combined effect of acid concentration and contamination from dissolved steel

The results of further tests relating to contamination from dissolved steel, shown in Fig. 8, illustrate the decrease in sensitivity with acid concentration. The tests were on 1 in. × ¾ in. samples of steel 3 in 80 ml. of the laboratory-reagent-quality acid at strengths from 50% to 70% HNO_3. Curve 1 shows the attack over the first 24 hr., and curves 2 and 3 show the attack in successive 24-hr. periods in these solutions. Curve 4 shows the results of 24-hr. tests in fresh acids with additions of ' used ' acid (*see*

* For this series of iron additions, 1 in. × ¾ in. samples of steel 1 were used in 80 ml. of acid.

Table IV

EFFECT OF ADDITION OF METALLIC IONS ON RESISTANCE OF 18/13/1 Cr–Ni–Nb STEEL IN 70% HNO_3

Solution	Equivalent Loss in Weight, g./sq. cm., to give Initial Metal Content	Loss in Weight, g./sq. cm., in 24 hr.
50 ml. used acid in 200 ml. fresh acid	0·0556	0·1050
20 ,, 230 ,,	0·0222	0·1137
10 ,, 240 ,,	0·0111	0·0958
5 ,, 245 ,,	0·0056	0·0537
2·5 ,, 247·5 ,,	0·0027	0·0111
1 ,, 249 ,,	0·0011	0·0044
Fresh acid only	0·0000	0·0016
0·067 g. pure nickel in 250 ml. acid	0·0111	0·0017
0·033 ,, ,,	0·0056	0·0013
0·016 ,, ,,	0·0027	0·0013
0·71 g. $Cr(NO_3)_3.9H_2O$ in 250 ml. acid	0·0111	0·0256
0·35 ,, ,,	0·0056	0·0129
0·18 ,, ,,	0·0027	0·0046
No addition	0·0000	0·0012
0·8 g. $Fe(NO_3)_3.9H_2O$ in 80 ml. acid	0·0100	0·0065
0·4 ,, ,,	0·0050	0·0009
0·08 ,, ,,	0·0010	0·0026
0·04 ,, ,,	0·0005	0·0007
0·1 g. pure iron in 80 ml. acid	0·0000	0·0011
No addition	0·0114	0·0009

Table IV) to give a dissolved steel content equivalent to 0·0111 g./sq. cm. for a 3 in. × 1 in. sample in 250 ml. of acid. Below 55% HNO_3 there is no indication of any serious complication in service from the effect of dissolved steel, but the danger sharply increases above 60% HNO_3.

These results on metallic contamination not only indicate the practical danger of allowing accumulations of dissolved steel in the 60–70% acid, but also show the great exaggeration of variability likely to arise from such a cumulative effect when carrying out tests in relatively small volumes of solution. Thus, although the primary cause of variability is most probably to be found in variable passivity effects, such as are frequently encountered with these steels in conditions of borderline severity, the practical effects of small initial attack may be very greatly increased, given favourable time/concentration conditions. Irregularity of the attacked surface, particularly when associated with a tendency to intercrystalline penetration, would be expected to give some initial increase in attack with time, even on a basis of increased effective surface area. There is ample indication that such penetration does promote a higher rate of attack. Where this increased attack eventually builds up sufficient dissolved steel in the test period to provide the necessary impetus, the rate of attack will increase very rapidly, and the combination of these factors accounts for the very variable results often obtained from cycle to cycle in the 48-hr. tests. To illustrate these effects a series of tests was carried out on steel 4. Duplicate 2 in. × ⅜ in. specimens, sawn from 1050° C. works-softened sheet, were emeried before test to produce a surface free from any prior penetration by chemical attack, and were tested in 80 ml. of boiling 70% acid (A.R.). The acid was changed at each weighing in a series of tests up to 144 hr., and the average rates of attack (g./sq. cm. per 24 hr.) for the various periods were as follows:

0–6 hr.	6–24 hr.	24–48 hr.	48–96 hr.	96–144 hr.
0·0004	0·0003	0·0007	0·0173	0·0380
0·0004	0·0003	0·0006	0·0427	0·0950

The samples were then tested in fresh acid for 48 hr., with intermediate weighings but without changing the acid; the rates of attack (g./sq. cm. per 24 hr.) were:

			Average Rates for Period:	
0–6 hr.	6–24 hr.	24–48 hr.	0–24 hr.	0–48 hr.
0·0070	0·0057	0·0424	0·0059	0·0241
0·0040	0·0037	0·0364	0·0038	0·0202

Finally, the samples were given successive cycles of 24 and 48 hr., each in fresh acid. The rates of attack (g./sq. cm. per 24 hr.) were 0·0294 and 0·0115 for 24 hr., and 0·0701 and 0·0820 for 48 hr.

The attack is much greater, even in the 6-hr. test, with a previously attacked sample. The much lower rates of attack in the broken 24-hr. and 48-hr. tests without change of acid, compared with the continuous 48-hr. runs, presumably indicate growth of passivity during the halts for weighing.

CONCLUSIONS

These tests on the behaviour of 18/13/1 Cr–Ni–Nb steel in boiling 70% HNO_3 have indicated a number of factors which must receive careful consideration, both in the interpretation of laboratory tests and in adjusting the service conditions to obtain the optimum service from the steel.

Grain Structure of the Steel—The attack in boiling concentrated nitric acid leads to some intergranular penetration, even with stabilized austenitic steels in a satisfactory condition regarding resistance to intercrystalline attack by other reagents. Penetration with these steels does not usually proceed to a depth of more than one or two crystals below the surface, but there is an indication that acceleration of attack from the small losses of the early stages is related to the development of this penetration effect. Large-grained structures may then suffer higher rates of attack, because of the more extensive removal of crystals for a given amount of boundary penetration.

Purity of the Acid—This is a most important aspect, and the presence of some substances can lead to very considerably increased attack.

(i) A supply of A.R. acid from one manufacturer was found to give a rate of attack about one-half of that produced by laboratory-reagent-quality acid from another source. A later supply from this source gave results of the same order as the A.R. acid. In all cases the amounts of checked impurities were very low. This aspect is not of great practical importance, because very-high-purity acid is probably not used in any industrial application; in any case, the difference in response was not large.

(ii) Of the acid radicals tested, the most objectionable was hydrofluoric acid; the addition of 0·1% by volume of concentrated (40%) acid produced acceleration of the order of six times in 48-hr. tests. Similar additions of phosphoric and sulphuric acids had relatively small effects, and with hydrochloric and nitrous acids no effect was observed.

(iii) Contamination from metallic radicals occurs as a result of solution of the steel, and can have a cumulative effect giving rise to a very serious acceleration of attack under suitable conditions. For this reason, certain tests in which the necessary accumulation of dissolved products can build up may greatly exaggerate much smaller effects from other causes.

Concentration of Acid—The effect of metallic contamination falls off very rapidly with decreasing concentration of acid, becoming negligible at 55% HNO_3. In practice, the effect is unlikely to be serious up to 60% HNO_3.

Passivity Effects—The results indicate the existence of variable passivity effects, with a tendency to a build-up of resistance during breaks in testing for reweighing. This can affect the response in the succeeding test cycle to a much exaggerated extent, by modifying the early rise in metallic contamination in a 48-hr. test.

Comparison of the results for 480-hr. tests with 18/9/1 Cr–Ni–Nb and 25/20 Cr–Ni steels with those for the 18/13/1 Cr–Ni–Nb material indicates a generally similar behaviour for all three materials in the 1050° C. air-cooled condition, with a possibly slightly lower overall resistance for the 25/20 Cr–Ni steel.

Acknowledgment

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Factors Influencing the Creep Resistance of Wrought Carbon Steels

By C. H. M. Jenkins, D.Sc., A.R.S.M., and H. J. Tapsell, A.C.G.I., M.I.Mech.E.

SYNOPSIS

This paper summarizes the work on the creep properties of carbon steels carried out for the Electrical Research Association at the National Physical Laboratory between 1929 and 1948. It includes a discussion on the influence of a number of manufacturing variables and other metallurgical factors on the creep rate, with particular reference to steels having abnormally high creep rates.

Introduction

This paper records points of interest arising from a series of investigations into the high-temperature properties of carbon steels carried out in the National Physical Laboratory during the years 1929–48.[1–11] The experimental work was undertaken for the J/E Committee on Steels for High Temperature Service of the British Electrical and Allied Industries Research Association, which is supported in this work by the British Iron and Steel Federation and other contributing bodies and firms. This paper is based on the more comprehensive account of the work given in B.E.A.I.R.A. Report No. J/T 139.[1]

The discovery at an early stage of the work of unusually high creep-rates in certain carbon steels showed that the investigations would be more extensive than originally assumed, and from time to time further studies were begun to explain new problems which had been brought to light. Creep resistance depends on attention to the relationship of grain size, heat-treatment, and abnormality. Gillett[14] ably summarizes many of the problems in this subject, and much progress has been made since the date of his paper. Epstein and Rawdon[15] discuss the properties of normal and abnormal steels shown by carburizing tests, but not in relation to creep properties. Grossman[16] refers to the relationship of abnormality in steels to the oxygen absorption of the steels during treatment in carburizing mixtures. Many grain-size effects are referred to in the literature on the subject.[13]

Carbon steels are used extensively in plant for high-temperature service, and will continue to be so used, as they possess an ease of fabrication combined with cheapness beyond the range of alloy steels. So long as the plant produced conforms closely during service to the design conditions, carbon steels will be used for resisting stress at moderately high temperatures in industrial plant. Alloy steels will, however, be used more for plant designed to operate at higher temperatures than in current use. The most efficient use should, nevertheless, be made of carbon steels.

In this paper the assessment of steels for high-temperature service is based on the results of tensile creep tests, but in service additional considerations must be taken into account. Other tests, including relaxation and combined-stress creep tests, have also been undertaken.[6, 7, 8, 9]

For the purposes of laboratory investigation a temperature of 450° C. was selected for the creep study as being near the maximum temperature at which steels can be used without the additional strength and oxidation resistance provided by alloying elements.

To expedite the work, which covered a large number of steels, a standard testing time of 2–8 days and a stress of 8 tons/sq. in. at 450° C. were chosen so as to produce fairly rapid comparative data. The working stresses have been estimated from tests at lower stresses and at other temperatures.[4, 5] The B.S.I. standard for boiler plates refers to proof creep-tests under these conditions, and in this report a creep rate exceeding 50×10^{-6}/hr. between one and two days defines a steel of poor creep resistance, designated 'abnormal.'

Information has been collected on the creep behaviour of carbon steel containing 0·10–0·42% of C in the form of castings, forgings, plates, pipes and tubes, which may be required to stay in service for 3–20 years.

Under service conditions loss of section may be caused by corrosion or erosion. Initially the effect on creep may be slight, but as small changes in stress cause large changes in creep rate, loss of section becomes progressively more important as corrosion proceeds. The deterioration of material in service, apart from oxidation, is associated with the rate at which structural changes proceed at the temperature of operation, which is in turn related to the creep properties. In a previous paper[11] the progress of spheroidization and graphitization of carbon steels was shown to be greatest in those which creep most rapidly. The progress of these changes and of oxidation ultimately leads to appreciable increase in creep rate.

SELECTION OF STEELS FOR EXAMINATION

Details of the steels examined in this investigation are given in Table I. The first three steels examined, Nos. 1–3, were specially made in a strictly similar and well-controlled manner with carbon contents of 0·13, 0·40, and 0·60%. Two ingots, each weighing 1·75 tons, were cast of each composition, and some were rolled to produce plates 1 in. thick. The 0·40% C

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Dr. Jenkins and Mr. Tapsell are on the staff of the National Physical Laboratory.

Table I

MANUFACTURING DETAILS OF STEELS GIVEN DETAILED STUDY

Steel No.	Steel Mark	Sources of Steel*	Designations Used in Earlier Papers	References to Literature	Creep Rate at 5 days 450° C./8 tons/sq. in. (normalized), millionths/hr.	Size As-Received	Casting Weight of Melt, tons	Size of Ingot, tons
1	2	3	4	5	6	7	8	9
		Tubes and Pipes made from B.O.H. Steels (normally produced in steelworks)						
52	KVA	Selected at random from production	...	5, 6	260	Tube 2 in. dia., $\frac{1}{8}$ in. wall thickness	66	3
84	LPS	One of 3 similar steels (84, 85, 86) showing similar characteristics. Each set of tubes was accompanied by 1 in. dia. hot-rolled bar from the same cast	...	...	240	Tube 2 in. dia. Bar 1 in. dia.	81	4·35
77	LFD	Selected at random from 6 steel tubes† supplied to a tube maker by different steel manufacturers, with creep rates of 137, 125, 134, 11, 100, 193, in normalized condition	...	...	137	Tubes 2 in. dia., $\frac{1}{8}$ in. wall thickness	63	3·15
81	LFH		...	5	100		128	2·8
35	KPJ	Cut from 10-in. dia. pipe	...	5	15	Pipe 10 in. dia.	...	...
		Bars made from B.O.H. Steels (normally produced in steelworks)						
93	HKE	Steel of rimming quality specially killed with Al	P	3, 4	140	Bar 1 in. dia.	76‡	≅2·5
64	LCW	With steel 65, selected from 11 B.O.H. steels obtained at random from production. Creep rates (normalized at 910° C.): 50, 2·5, 11·7, 14, 4·6, 3·1, 6·5, 2, 46, 4·4, 9·0 (av. 14): as-received (hot-rolled): 1·3, 2·0, 1·2, 2·5, 2·3, 3·1, 0·4, 1·2, 5, 1·5, 6·4, (av. 2·5)	...	...	50	Bars 1 in. dia.	77	3·75
72	LDE		...	...	46		80	4·35
67	LCZ		...	...	14		81	3·75
97	NGK	Taken at random from production	...	10, 11	11	Bar $\frac{3}{4}$ in. dia.	70	...
65	LCX	(*See* above *re* steels 64, 72, and 67)	...	...	2·5	Bar 1 in. dia.	85	3·75
94	JCN	Steel of rimming quality specially killed with Si, so as to be a counterpart of steel 93	...	6, 9	1·7	Bar 1 in. dia.	75	≅3
		Plates made from Basic Electric Steels (specially produced in steelworks)						
2	EVN 3–4	Produced by one company in an arc furnace under similar conditions, with C contents of 0·13% (1) and 0·4% (2)	B	2, 3, 4, 10	19	Plates 1 in. thick	3·5‡	≅1·75
1	EVN 1–2		A	2, 3, 4, 11	2·5			
20	GUF	Produced by another firm, with C content of 0·20%	H	2	1·4		3·4	≅0·8
		Pipes made from A.O.H. Steels (selected from material being made for a power plant)						
75	LFA	Cut from 12-in. dia. pipe (superheater header)	...	5, 6, 9	3·2	Pipe 12 in. dia.	...	...
		Bars made from A.O.H. Steels (specially produced in steelworks						
88	LTR	Made from one cast of steel treated with Fe–Si (steel 89). Al was added during teeming to one ingot only (steel 88)	...	...	49	Bars 1¼ in. dia.	47‡	1·35
89	LTS		...	...	4			
		Plates made from A.O.H. Steels (specially produced in steelworks)						
15	GBE 8–14	Steels 15, 19, and 21: low-carbon steels; steels 9, 10, and 14: 0·4% of C. Steels 14 and 15 were plates forged from a portion of a cogged ingot. The plates were made for boilers and general engineering purposes. Steel 19 was cut from a hollow forged drum, and steel 10 was a portion of a forged disc	E	2, 3, 4, 14, 17, 18	23	Plate 1 in. thick	36	≅36
9	FLE		K	2, 3, 4, 6	6·8		36	1·3
10	FNW		L	2, 3, 4	5·0	Bar 1¼ in. square	46	≅11
14	GBE 1–7		J	2, 3, 4, 6, 10	3·1	Plate 1 in. thick	29	≅3
19	GTM		G	2	2·0	Plate 1¼ in. thick	37·5	24
21	GVB		F	2, 3, 4, 6	1·5	Plate 1 in. thick	37	0·8 and 1·3

* Made by nine manufacturers who reported 32–75% use of scrap in the open-hearth charges

† 0·35–0·57% Mn, 0·009–0·070% Si. Although two had higher Mn contents than steels 77 or 81 (0·38 and 0·35% respectively), their rates of creep were intermediate (125 and 134)

‡ Cast material from these charges was also supplied

steel was found to be appreciably weaker in creep than the correspondingly normalized 0·15% C steel, and the cause of this difference was immediately investigated. Extensive work was not carried out on the 0·60% C steel as the influence of carbon content became of less interest than variations in the creep behaviour of several similar low-carbon steels. Further critical experiments were therefore planned to study the effect of composition, heat-treatment, grain size, and microstructure, and to determine the long-time creep properties of various carbon steels in production.

Table I contains a summary of the creep strength of 37 steels obtained from nine manufacturers. Some of the steels were not specially made for high-temperature service, and a few others were produced in an unusual manner to permit study of a particular aspect of the deoxidation technique. Altogether in this table there are :

11 tubes and pipes in B.O.H. steels
14 bars " " "
3 plates in basic electric steels
1 pipe (superheater header) in an A.O.H. steel
2 bars in A.O.H. steels
6 plates " "

In addition, 23 A.O.H. steels from boiler-drum forgings in current production in 1938 were examined to give an independent assessment of creep strength and grain size[1] ; they were found to be remarkably similar in behaviour and properties. Steels with 0·60% of C and above have also been studied.[1, 11]

Of the 65–70 casts examined, about 50 were the result of normal production in steelworks between 1929 and 1939. The remainder were either specially produced in normal-sized furnaces or were specially treated with deoxidants before casting. The melts varied between 3·4 and 128 tons in weight, and the minimum ingot weight was 0·8 ton.

Twenty-four of these steels, representing a particular type or exhibiting special characteristics, were selected for more detailed study, and the results are briefly given in Tables II, III, V, and VII. The steels in

Table II

COMPOSITION OF THE STEELS**

Italic figures show makers' analyses

Steel No.	C, wt.-%	Si, wt.-%	Mn, wt.-%	S, wt.-%	P, wt.-%	Cr, wt.-%	Ni, wt.-%	Cu, wt.-%	Al, wt.-%			Analysis of Vacuum-Fusion (Carbon Reduction) Process[10–11]		
									Soluble	Insoluble	Total	O_2, wt.-%	N_2, wt.-%	H_2, wt.-%
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10a)	(10b)	(10c)	(11)	(12)	(13)
52	*0·12*	0·07	*0·45*	*0·027*	*0·017*	0·08	0·06	0·09	0·014	0·004	0·018	0·003	0·003	0·00011
84	0·13	0·06	0·49	0·021	0·014	0·08	0·07	0·07	0·042 (tube)	0·004 (tube)	0·046 (tube)	0·002 (bar)	0·004 (bar)	0·00005 (bar)
93	0·16	0·005	0·46	0·032	0·028	0·07	0·17	0·19	0·024	0·010	0·034	0·004–0·007	0·003	0·00005 (average)
77	*0·10*	0·015	*0·38*	*0·036*	*0·016*	0·07	0·05	0·05	0·004	0·009	0·013	0·005	0·003	0·00006
81	*0·11*	*0·04*	*0·35*	*0·038*	*0·032*	0·10	0·04	0·02	0·003	0·002	0·005	0·008	0·002	0·00004
64	*0·14*	0·16	*0·76*	*0·042*	*0·022*	0·05	0·05	0·08	0·016	0·005	0·021	0·008	0·004	Trace
88	0·21	0·26	0·56	0·027	0·035	0·05	0·02	0·07	0·010	0·012	0·022	0·017	0·002	0·00005
72	*0·20*	0·15	*0·58*	*0·028*	*0·016*	0·05	0·08	0·17	0·015	0·010	0·025	0·013	0·003	0·00015
15	0·19	0·08	0·40	0·040	0·051	0·15	0·07	0·09	0·001	<0·001	<0·002	0·007	0·003	0·00012
2	0·40	0·21	0·59	0·038	0·033	0·07	0·03	0·08	0·010	0·005	0·015	(0·003) †	...	...
35	*0·135*	*0·18*	*0·47*	*0·037*	*0·028*	0·02	0·02	0·06	0·002	<0·001	<0·003	0·005	0·002	0·00006
67	*0·19*	0·15	*0·78*	*0·029*	*0·017*	0·05	0·07	0·15	0·010	0·010	0·020	0·017	0·004	0·00005
97	0·17	0·05	0·63	0·032	0·016	0·01	0·03	0·09	0·004	0·003	0·007	0·022	0·003	0·00006
9	0·42	0·31	0·50	0·031	0·031	0·07	0·09	0·06	0·002	<0·001	<0·003	(0·008) †	...	...
10	0·40	0·16	0·53	0·041	0·042	0·08	0·05	0·12	0·002	<0·001	<0·003	(0·002) †	...	...
89	0·22	0·24	0·56	0·029	0·035	0·05	0·02	0·07	0·001	<0·001	<0·002	0·011	0·002	0·00004
75	*0·24*	*0·10*	*0·61*	*0·032*	0·040	0·02	0·03	0·09	0·002	<0·001	<0·003	0·008	0·002	Nil
14	0·40	0·21	0·58	0·037	0·035	0·01	0·02	0·06	0·001	<0·001	<0·002	(0·003) †	(0·003) †	(0·00003) †
65	*0·25*	*0·20*	0·74	*0·032*	*0·043*	0·06	0·08	0·08	0·003	0·006	0·009	0·004	0·004	0·00003
1	0·13	0·18	0·53	0·038	0·029	0·03	0·08	0·08	0·004	<0·001	<0·005	0·009	0·003	0·00009
19	0·16	0·14	0·66	0·037	0·034	0·02	0·08	0·05	0·001	<0·001	<0·002	0·006	0·003	0·00006
94	0·17	0·20	0·72	0·024	0·022	0·08	0·06	0·11	<0·001	0·006	<0·007	0·012*	0·004*	0·00002*
21	0·15	0·28	0·76	0·028	0·030	0·08	0·09	0·11	0·003	0·001	0·004	0·016	0·004	0·00006
20	0·20	0·20	0·56	0·023	0·011	Trace	0·16	0·10	0·006	0·005	0·011	0·005	0·010	0·00008

* On ¼ in. dia. re-rolled bar † 0·4% carbon steels ** The molybdenum and vanadium contents are all below 0·01%

these and subsequent tables are arranged in order of descending creep-rate based on tests at 450° C. under a stress of 8 tons/sq. in. at 5 days. This arrangement was adopted because it readily correlates the high creep-rate in normalized steels with the fineness of grain size and degree of abnormality disclosed by the McQuaid–Ehn test. This correlation occurs with the samples normalized from 900–950° C., but not with the untreated as-received or hot-worked steels.

Tests were also carried out at 400° C. under a stress of 15 tons/sq. in. and at 550° C. under 4 tons/sq. in. The results of these tests, given in column 7 of Table V, show that the steels are markedly different in creep behaviour and are arranged in the same order as in the tests at 450° C.

EFFECT OF COMPOSITION

Particulars of the process of manufacture and the conditions of melting and deoxidation, factors influencing the final composition of the steels, are given in Table III, which also contains the chemical composition of the steels and the results of the vacuum-fusion (carbon reduction) method of determining the oxygen, hydrogen, and nitrogen contents.

The steels contain: 0·01–0·08% of Cr; 0·02–0·09% of Ni (in one case 0·17); 0·02–0·19% of Cu; and less than 0·01% of Mo or V. The nitrogen contents are fairly constant between 0·002–0·004%, and the hydrogen between 0·00003–0·00015%.

Table III
PROCESSING OF THE STEELS

Steel No. (1)	Process of Manufacture (2)	Condition of Bath (3)	Method of Deoxidation (4)	Total Si Addition, % (5)	Total Al Addition, lb./ton (6)	Notes 7
52	B.O.H.	N	Al–Si alloy and Fe–Mn to ladle	0·07	2·5	Soluble Al high
84	B.O.H.	N	Balanced steel, Al, Fe–Si, Fe–Mn, and spiegel added	0·05	2·25–2·37	Soluble Al high
93	B.O.H.	Not M	Steel not made in usual way for tubes, rimming quality	...	1	Soluble Al high. Higher oxygen than 52 or 84 makes insoluble Al high
77	B.O.H.	N	Treated with Fe–Mn and Al; Si not added	Nil	1·56	Insoluble Al high, Si low
81	B.O.H.	M	Treated with spiegel and Fe–Mn; Al added	0·06	0·75	Low Si, Mn and low Al, (*see* 77)
64	B.O.H.	N	Treated with Si alloy, 80% Si, spiegel, and Fe–Mn	0·16	0·37–0·50	Si, Mn, Al higher than 81
88	A.O.H.	M	Killed in bath by Si–Mn and Fe–Mn; Al added to ladle	0·14	1	Si, soluble and insoluble Al high, oxygen high
72	B.O.H.	N	Treated with Si alloy, 80% Si, spiegel, and Fe–Mn	0·15	0·37–0·50	Si addition influenced Al and oxygen
15	A.O.H.	M	Treated with Fe–Si and Fe–Mn	0·13	...	Low Al confirms absence of Al addition
2	Basic electric	M	Al added to ladle	(Not known)	0·15	(*Cf.* 1.) Relatively high Al
35	B.O.H.	N	Fe–Mn to bath, Al and alsifer to ladle	(Not given)	(Not given)	Low Al
67	B.O.H.	N	Treated with Si alloy, 80% Si, spiegel, and Fe–Mn	0·15	0·37–0·50	Less soluble Al than 72 or 64, high oxygen
97	B.O.H.	N	Spiegel, Fe–Mn, and Fe–Si added	0·06	(Not given)	High oxygen, low Al and Si
9	A.O.H.	M	Fe–Mn, Fe–Si, and Fe–Ti added	0·45	...	Low Al, high Si
10	A.O.H.	M	Fe–Mn added	...	...	Low Al and oxygen
89	A.O.H.	M	Killed in bath by Si–Mn and Fe–Mn	0·14	Nil	Low Al, high oxygen
75	A.O.H.	N	Si-killed	(Not given)	(Not given)	Low Al and moderate Si
14	A.O.H.	M	Fe–Si and Fe–Mn added	0·11	...	Low Al and oxygen
65	B.O.H.	N	Fe–Si, spiegel, Fe–Mn, and 88% purity Al added	0·22	0·5–0·62	Si addition has caused Al retention
1	Basic electric	M	Al added to ladle	(Not known)	0·15	(*Cf.* 2)
19	A.O.H.	M	Fe–Si, Si–Mn, Fe–Mn	(Not known)	Nil	Low Al and oxygen
94	B.O.H.	M	Fe–Si treated	0·24	0·25–0·37	Si addition made insoluble Al high
21	A.O.H.	M (nearly)	Si–Mn and Fe–Mn treated. Al added	0·45	0·5	Al and Si additions high but residual Al low because steel-deoxidized oxygen high
20	Basic electric	M	Si and Fe–Mn, alsimin, and Al	0·31	1·5	Insoluble Al high. Heavy addition of Si has counteracted heavy Al addition

M = dead-melted N = not recorded

Carbon

The steels principally considered in this summary have carbon contents of 0·10–0·42%, and no appreciable improvement in the long-time creep strength can be traced to an increase of carbon content, *i.e.*, other conditions in the production of the steels have produced much larger effects. It has been shown[11] that, although increases in carbon content up to 1·1% cause an increase in the yield point and ultimate stress at both room temperature and 450° C., the creep strength was more or less independent of the carbon content between 0·16–1·1% at temperatures between 450° and 650° C.

Manganese

The average Mn content of the five B.O.H. steels at the top of Tables II and III which have creep rates of 100×10^{-6}/hr. or greater at 450° C. under 8 tons/sq. in. stress is 0·43%. The remaining 19 steels in these tables with creep rates of less than 100×10^{-6}/hr. have Mn contents between 0·47–0·78% (average 0·61%) distributed in a random manner in the various steels made by the A.O.H. (9), B.O.H. (7), and B.E.F. (3) processes (the figures in brackets indicate the number of steels selected which were melted in furnaces of that type).

The average Mn content of 23 A.O.H. forgings which have an average creep-rate of $1·5 \times 10^{-6}$/hr. at 5 days under the standard test was 0·65%. The carbon contents of these steels were mostly between 0·21–0·25%, the nickel 0·24–0·06%, and the chromium 0–0·19%.

In a previous paper[11] it was shown that certain steels of high carbon content which were low in Mn showed high rates of spheroidization and graphitization and very poor creep properties, but in steels containing about 0·70% of Mn the creep strength was good and similar to that of steel 14. The evidence suggests that a Mn content of $\geqslant$ 0·6% is preferable.

Silicon

The average Si content of the five B.O.H. steels with creep rates of 100×10^{-6}/hr. or above was 0·04%. The remaining 19 steels in Tables II and III had contents between 0·05–0·31% (average 0·18%), again distributed in a random manner among A.O.H. (9), B.O.H. (7), and B.E.F. (3). Columns 4 and 5 in Table III give the particulars of the total Si additions to the steels, from 0–0·45%. The average Si content of the 23 A.O.H. forgings was 0·21%.

Plotting the Si content against the creep rate of 65 carbon steels shows a general relationship roughly parabolic in shape. Steels containing up to 0·05% of Si show a very high creep-rate, but those with 0·20% or more have in general a good creep resistance if other factors are favourable. Sufficient Si is not present for it to be regarded as an alloying element, but, owing to the process used in manufacture, when the Si content is low the Al content is often high and the Mn low.

Silicon does not completely deoxidize a steel but, as discussed in the following section, a low oxygen content is not necessary or desirable for good creep resistance, and attempts to obtain low values may weaken the steel.

Aluminium and Oxygen

Column 6 in Table III shows the amount of Al added to the various steels, and columns 10*a* and 10*b* of Table II show the proportions in the steels in the soluble and insoluble forms respectively. From these figures it is apparent that the use of large quantities of Al induces a high creep-rate, and so its use should be restricted in steels intended for applications where creep resistance is important.

Additions of Al of 1–2½ lb./ton were made to some of the B.O.H. steels that exhibited the highest creep-rates, and it is clear that under the melting conditions in use at the date of production of some of these steels, the amounts added were harmful to the creep properties. The damage may either be due to the absence of oxygen or to the presence of Al in some particular form, but these two factors may be inter-related.

Aluminium additions should probably not exceed 0·5 lb./ton if a creep rate of less than 2×10^{-6}/hr. under a stress of 8 tons/sq. in. at 450° C. is constantly required. If, however, the manufacturing conditions are well controlled, additions of Al of up to 1½ lb./ton can be given without the creep rate exceeding 50×10^{-6}/hr. after 2 days' testing. The steels should in addition contain suitable proportions of Si and Mn (probably not less than 0·13 and 0·60% respectively).

In the present work the analysis of the steels for oxygen, hydrogen, and nitrogen contents has been made by the vacuum-fusion (carbon reduction) technique.[18–22] The residual oxygen appears to be related to the creep properties.

The oxygen contents of the B.O.H. steels which show a good creep strength, with one exception, have been found to be at least 0·010%, while the steels of poor creep strength, *i.e.*, with a creep rate of 50×10^{-6}/hr. or higher, have oxygen contents not exceeding 0·008%. The 0·4% C steels of either the B.O.H. or A.O.H. types have lower oxygen contents than steels with less carbon, *i.e.*, between 0·15–0·20%. This is probably caused by the reducing action of the greater amount of carbon.

Table IV—EFFECT OF HEAT-TREATMENT ON ALUMINA CONTENT AND CREEP RATE

Steel No.	Normalized			Treated at 1100° C. for 6 hr.		
	Soluble Al, %	Insoluble Al, %	Creep Rate, millionths/hr.	Soluble Al, %	Insoluble Al, %	Creep Rate, millionths/hr.
93	0·027	0·010	120 (at 950° C.)	0·024	0·010	5·6
88	0·009	0·013	49 (at 910° C.)	0·010	0·012	3·7
89	0·001	<0·001	2·9 (at 910° C.)	0·001	<0·001	3·6
94	<0·001	0·003	1·0 (at 950° C.)	<0·001	0·006	1·3

In the B.O.H. steels killed with a fairly heavy dose of Al, the oxygen is insufficient to use all the Al, and the surplus is left in the steel.

The low-carbon A.O.H. steels have oxygen contents between 0·007–0·017%, and their creep rates are somewhat lower than those of the B.O.H. steels.

A test was carried out to determine whether the oxygen and carbon contents would be reduced on long heat-treatment by interaction of these two elements. A trial bar of steel 94 was examined before and after heating to 1100° C. for 15 min., and then at 650° C. for 60 days. The oxygen content remained unaltered

Table V

CREEP RATE IN THE AS-RECEIVED AND NORMALIZED CONDITIONS, AND GRAIN-SIZE DETERMINATIONS AFTER TREATMENT AT 900–950° C.

(Creep rate, millionths/hr., grain size in A.S.T.M. numbers)

Steel No.	Condition as Manufactured: Creep Rate at 8 days (hot-worked)	Tests under 8 tons/sq. in. at 450° C.				Creep Rate	Steels Treated at Normalizing Temp. (15 min. at temp.)	McQuaid–Ehn Test	
		Normalizing Temp. (A.C. after 15 min.), ° C.	Normalized Specimens, Creep Rate				W.Q. Austenite Grain Size on Wedge-Shaped Specimens	Condition of Pearlite[a] and Grain Size (by counting) (A = abnormal, N = normal)	Range of Grain Size by Grids
			at 5 days	at 8 days	at 20 days				
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
52	81	950	260	260	...	...	8	Equally A and N 3–4	0[i]–7
84	Bar 1·1	950	...	240	...	...	8	A 8[h, j]	Many areas do not show grain boundaries
	Tube 173	950	240	246	...	...			
93	6·5	950	140	120[b]	107[e]	120[n]	8	Markedly A 8[h, k]	
77	90	950	137	90	...	...	5–6	Equally A and N 4	2–5
81	63	950	100	73	...	...	4	(Slightly A) N 4	2–6
64	1·3	910	50	40	...	713[p]	8+	A 6–7	5–8
88	2·0	910	49[c]	49	...	...	7–8[l]	Equally A and N 4	2[l]–7
72	5·0	910	46	...	...	416[p]	8	A (Slightly N) 6–7	5–8
15	7·6	950	23	16·5	10·8	90[n]	3–4	N 2–3	2–5
2	1·0	900	19	18·6	18·5	...	7–8	A 6–7	4–7
35	9	950	15 and 11·6	10	...	...	...	... 3	2–4
67	14	910	14	...	...	...	7	A (inside) 6–7 N (outside)	Fairly uniform
97	10·5	950	11	11	10[f]	37[n]	4–5	N 3	2–5
9	4·2	900	6·8	4·2	2·1	35[p]	5–6	N 3	1–4
10	12	900	5·0	2·0	1·5	...	4	N 3–4	2–5
89	2·4	910	4·0[d]	2·9	...	...	6[m]	N 4	3–6
75	3·5	925	3·2	2·1	...	...	...	... 3	3
14	1·3	900	3·1	2·6	1·7	...	6	N 3–4	2–6
65	2·0	910	2·5	...	...	23[p]	6–7	N 3	2–5
1	3·7	950	2·5	1·8	1·3	...	5	N 2–3	1–5
19	...	950	2·0 and 1·0	0·8	0·6	...	...	... 1	1
94	1·0	950	1·7	1·0	0·4[g]	15[n]	5	N 4	2–6
21	0·7	950	1·5	1·25	0·8	...	5	N 4	3–6
20	...	950	1·4 and 0·9	0·8	0·8 and 0·25	...	...	N 3	0–6

[a] See Ref. 15.
[b] After 900° C./½ hr. A.C. creep rate 160 at 4 days; after 950° C./½ hr. A.C. creep rate 110 at 8 days; after 1000° C./½ hr. A.C. creep rate 47 at 8 days
[c] After 950° C./15 min. A.C. creep rate 13·7 at 5 days and 11 at 8 days; after 975° C./15 min. A.C. creep rate 8·5 at 5 days and 8·5 at 8 days; after 1000° C./15 min. A.C. creep rate 2·8 at 5 days and 1·6 at 8 days.
[d] After 950° C./15 min. A.C. creep rate 2·5 at 5 days and 2·0 at 8 days; after 975° C./15 min. A.C. creep rate 4·9 at 5 days and 4·0 at 8 days
[e] Total elongation 7·02% in 20 days
[f] Total elongation 0·96% in 20 days
[g] Total elongation 0·12% in 20 days
[h] Difficult to determine as boundaries are incomplete
[i] Mixed grain size
[j] 8 hr. at 927° C. in vacuum and quenched shows austenitic grain size 6–8
[k] 8 hr. at 927° C. in vacuum and quenched shows austenitic grain size 0–6
[l] 15 min. at 950° C. grain size 5–6
[m] 15 min. at 950° C. grain size 4
[n] 400° C. 15 tons/sq. in. on normalized specimens at 8 days
[p] 550° C. 4 tons/sq. in. on normalized specimens at 3 days

at 0·012%, although 0·17% of C was present.

Sound ingots can be produced in A.O.H. steels without using Al, and its addition is not customary. In an A.O.H. steel (88) purposely killed with Al the oxygen content showed an apparent increase and the steel was made abnormal in creep by the Al addition.

The soluble and insoluble aluminium contents of all the steels were determined as follows:

(1) Ten g. of sample taken. The soluble portion was that extracted by a solution of 50% HCl (vol./vol.) and the insoluble was that retained in the residue after solution of the steel. The residue in the insoluble portion was that taken into solution by fusion with potassium bisulphate. The greater part of the iron was separated by another separation.

(2) The remainder of the iron was removed by extraction of the iron with 'cupferron' complex at *p*H 0·6.

(3) The Al content was determined colorimetrically with aluminon (aurin tri-carboxylic acid).

The results are given in columns 10*a* and 10*b* of Table II.

The steels used for the determinations were in the form of 1-in. dia. bars heat-treated at 1100° C. for 6 hr. and cooled in air. This heat-treatment was undertaken to dissolve as much as possible of the alumina, or other compounds, in the steel, and thus raise the soluble Al figure. Four check tests were made to ascertain the effect of this treatment. The results given in Table IV do not indicate any marked solubility effect, although the creep rate has been greatly changed.

The amount of Al retained in the steels after deoxidation and casting is mainly related to the amount added (*see* column 10*c* of Table II), but Si causes a greater retention of Al owing to the supposed formation of aluminium silicate, which does not rise rapidly in the molten steel. The proportions of oxygen and Mn in the molten steel at the time of the addition of the Al exert appreciable but opposite effects on the amount of Al required to render the steels suitable for casting.

Other effects, such as the variation of the time of addition of Al in the melting procedure, whether the steel was dead-melted, and whether the furnace had an acid or basic lining, must also be considered when the study of the effect of Al is assessed. Even a higher carbon content may help to reduce the oxygen content. Owing to the higher operating temperature reactions proceed more to completion in an electric than in an open-hearth furnace, but it should be noted that a low oxygen content may not be desirable from the creep-resistance point of view. Dead-melting before deoxidation reduces the oxygen content, and thus the subsequent Al addition. If silica is formed either during dead-melting or from oxygen pick-up during casting, it is likely to interfere with the free separation of the alumina from the melt. Other oxides may equally well attach themselves to the SiO_2 particles. Two A.O.H. steels were deoxidized with Al, and in both the SiO_2 could not float out of the steel, whereas in a comparable untreated sample it was able to float into the molten slag in the ladle and be removed (steel 89). This accounts for the apparent anomaly of the rise in oxygen content on the addition of a deoxidant. The attachment of the Al_2O_3 to SiO_2 has also been noted in the B.O.H. steels containing appreciable silicon.

In the oxide and insoluble residue of Al-killed steels isolated by solution of the iron by alcoholic iodine, the presence of compounds of Al with nitrogen and carbon has been detected (perhaps AlN and Al_4C). Further work, including X-ray studies, on these residues is desirable, for these compounds may play an important part in determining the structural characteristics of the iron carbide on heat-treatment.

The abnormality which appears to be prevalent in steels made by the B.O.H. process might be explained by the suggestion that the carbide or nitride may be largely or partly present as a second phase with austenite in the region 900–950° C., but can be taken wholly into solid solution in the austenite on raising the temperature above 950–1050° C. On cooling, the Fe_3C which separates out may be affected by the Al compound, which influences the form of the pearlite. In A.O.H. steels the action of the oxygen content may be somewhat different, as the resulting SiO_2 or silicate material may link itself in the solid state with the aluminium carbide, thus hindering the ready solution and precipitation of the carbide in the metal. If this could be conclusively proved it would be another example of the general hypothesis that fine particles obstruct grain growth.

PROPERTIES OF STEELS IN THE AS-RECEIVED AND NORMALIZED CONDITIONS

Table V sets forth the data obtained, which show the possible relationship between the creep properties of the steel and the austenitic grain size at normalizing temperatures (900–950° C.). The form of the carbide structure in the McQuaid–Ehn test is given in column 9.

The steels intended for creep tests were heated at a conveniently rapid rate to 650° C., and above this at a rate of 5° C./min. until the heat-treatment temperature was attained.

The steels may be divided broadly into two classes:

(1) Those which have good creep-resistance as-received, and retain this after normalizing. These are generally A.O.H. steels, but include some B.E.F. and B.O.H. steels.

(2) Those which may have either good or bad creep-resistance as-received, but have bad creep-resistance when normalized between 900–950° C. These are generally B.O.H. steels, often deoxidized with high proportions of Al, and show abnormal characteristics in the McQuaid–Ehn test.

Low temperatures of normalizing do not lead to the development of the best creep-resistance of the steels, particularly those normally having poor creep-resistance in the heat-treated condition. The effect of higher normalizing temperature is described in the footnotes to Table V relating to steels 93 and 88. The abnormal steel 93 shows marked improvement in strength after treatment at 1000° C. Steel 88, which is weaker in creep, but would not be classified as abnormal, is greatly improved after treatment at 1000° C.

INFLUENCE OF MODE OF MANUFACTURE

Steels produced by the A.O.H. process have in general good creep-resistance in the as-received and

Table VI

DISTRIBUTION OF STEELS ACCORDING TO CREEP RATE

Type of Steel	No. of Samples Tested	Creep Rate at 5 Days (8 tons/sq. in. and 450° C.), millionths/hr.			
		Below 2·5	2·5–10	10–100	Above 100
As-Received					
B.O.H.	29	9	7	6 (4)*	7 (5)*
A.O.H.	8	2	4	2	...
B.E.F.	2	1	...	1	...
Normalized					
B.O.H.	29	4	8	9	8 (8)*
A.O.H.	32	25	7	...	...
B.E.F.	3	1	2	...	...

* Figures in brackets represent the number of steels supplied in the form of tubes

normalized conditions, but there is much scatter in the results for B.O.H. steels. An analysis of the results according to the creep rate (*see* Table V) is given in Table VI.

With samples of a tube and of a bar steel obtained from the same cast, the bar sample had good and the tube poor creep-resistance as manufactured, but normalizing produced a poor creep-resistance in both. Several tube-working processes are in use, and this is the result of only one of these processes; other processes may have different effects. Furthermore, some of the hot-working processes may begin at 1100–1150° C., and even the finishing temperature of a hot-rolled tube or bar may be higher than that of a subsequent normalizing process. The grain-coarsening effects produced at the hot-working temperatures are probably not eliminated unless the final rolled product is normalized. The effect of large reductions may, however, persist even after subsequent heat-treatments.

Samples from each of the 24 selected steels were microscopically examined to supplement the creep tests. The structure of 20 in the as-received and normalized conditions, arranged in order of descending creep-rate of the latter, are given in Figs. 1 and 2. The austenitic grain size of samples W.Q. from the normalizing temperature is recorded in Table V, column 8; the steels of high creep-rate have a fine grain size, 8 on the A.S.T.M. scale, and those of low creep-rate have a grain size of 5 or below.

MCQUAID–EHN GRAIN SIZE

Columns 9 and 10 of Table V contain the McQuaid–Ehn grain sizes after carburizing for 8 hr. at 927° C. Grain size is expressed in terms of the standard A.S.T.M. scale, together with the ranges proposed by the N.P.L. to define intermediate ranges such as 4–5.*

* The A.S.T.M. count for grain sizes 4 and 5 refers to material containing 80,000 and 160,000 grains/sq. in. respectively. No mention of the range of sizes tolerated or the meaning of the size 4–5 often recorded has been given. It is now suggested[1] that grain sizes 4 and 5 are used to cover 70,000–100,000 and 140,000–200,000 respectively, and the sizes 4–5 used for the range 100,000–140,000.

The condition of the pearlite and the fineness of the grain size both give useful information when considered in relation to the creep rate.

The table indicates a transition between abnormal and normal grain size at a creep rate of about 20×10^{-6}/hr. for normalized samples, but the upper limit of creep rate for a very good steel is probably about 3×10^{-6}/hr. at 8 days under a stress of 8 tons/sq. in. at 450° C.

The following remarks are the results of observations on the full number of steels, 65 in all:

(1) All normalized steels with creep rates of 11×10^{-6}/hr. or less under a stress of 8 tons/sq. in. at 450° C. had normal pearlitic structures according to the McQuaid–Ehn test. The highest creep-rate of a steel which showed a wholly lamellar pearlitic condition was 23×10^{-6}/hr.

(2) All steels with creep rates of 140×10^{-6}/hr. or above showed a wholly abnormal pearlitic condition. The lowest creep-rate found in a steel with this condition was 19×10^{-6}/hr.

(3) Steels with creep rates between $11 \cdot 7$–137×10^{-6}/hr. were on the whole those which showed mixed normal and abnormal characteristics. A number of steels in this range exhibited either purely normal or purely abnormal carbide conditions. The dividing line might be about 20–25×10^{-6}/hr. under the standard conditions for creep tests.

Further heat-treatments were carried out on some of the McQuaid–Ehn specimens shown in Fig. 3, to clear up points of interest appearing in steels 52, 84, 93, and 94, which might be exceptions to the general behaviour. The experimental work[1] shows on the whole that the temperature and time selected for the McQuaid–Ehn test were suitable for a wide range of steels.

COMPARISON OF PROPERTIES OF VARIOUS STEELS

The comparison of certain steels throws light on the special problems introduced by differences in the methods of deoxidation and production.

Steels 1 and 2

These contained 0·13 and 0·40% of C respectively; they were produced in the basic electric furnace under strictly comparable conditions and were killed with 0·15 lb. of Al per ton. Both steels contain the same proportions of oxygen, between 0·003–0·004%, but the amounts of soluble Al and its compounds, and of insoluble Al_2O_3, are noticeably less in steel 1 than in steel 2, being 0·004% soluble and $< 0 \cdot 001\%$ insoluble compared with 0·010% and 0·005% respectively. Steel 2 showed a fine McQuaid–Ehn grain size but a relatively high creep-rate of $18 \cdot 6 \times 10^{-6}$/hr. at 8 days under 8 tons/sq. in. at 450° C. in the normalized condition. Steel 1 had, under similar test conditions, a creep rate of $1 \cdot 8 \times 10^{-6}$/hr.

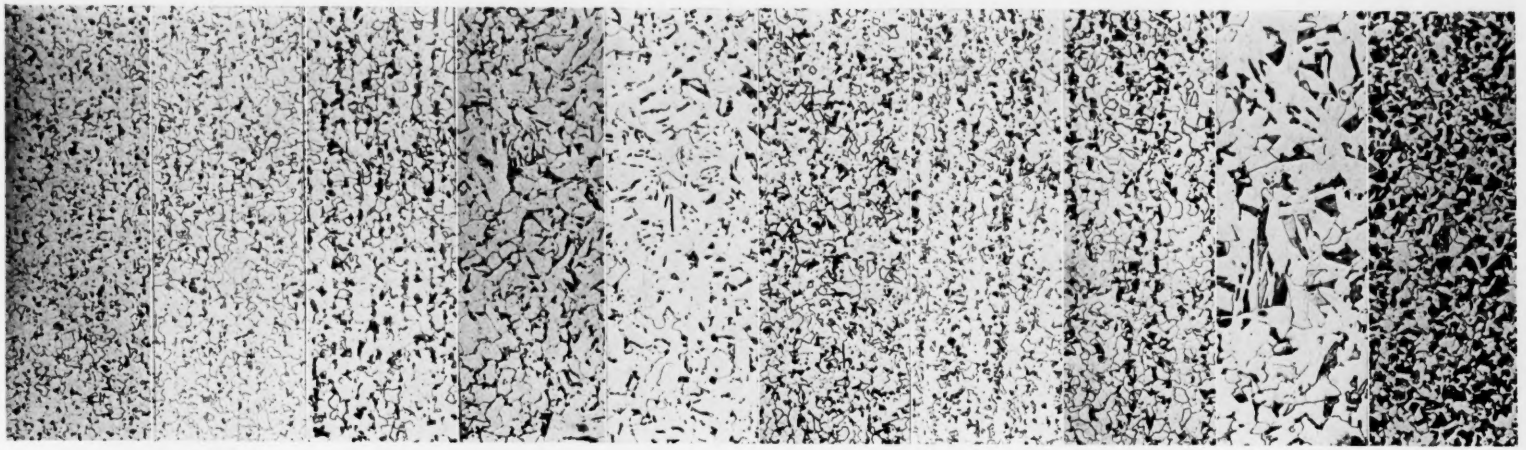
Steels 93 and 94

These two steels were similarly made in a B.O.H. furnace and were of rimming quality. Steel 93 was, for experimental purposes, exceptionally deoxidized with 1 lb. of Al per ton, and steel 94 was treated with

Fig. 1 *a-t*—Steels in as-received condition, arranged in order of increasing creep-strength. The numbers refer to the steel numbers and (in brackets) to the creep-rate in millionths/hr. at 5 days at 450° C., 8 tons/sq. in. × 150, reduced by ⅓ linear in reproduction

[*Jenkins and Tapsell*
[*To face p.*366

(a) 52 : 950, 260 (b) 84 tube : 950, 240 (c) 93 : 950, 140 (d) 77 : 950, 137 (e) 81 : 950, 100 (f) 64 : 910, 50 (g) 88 : 910, 49 (h) 72 : 910, 46 (i) 15 : 950, 23 (j) 2 : 900, 19



(k) 67 : 910, 14 (l) 97 : 950, 11 (m) 9 : 900, 6·8 (n) 10 : 900, 5·0 (o) 89 : 910, 4·0 (p) 14 : 900, 3·1 (q) 65 : 910, 2·5 (r) 1 : 950, 2·5 (s) 94 : 950, 1·7 (t) 21 : 950, 1·5

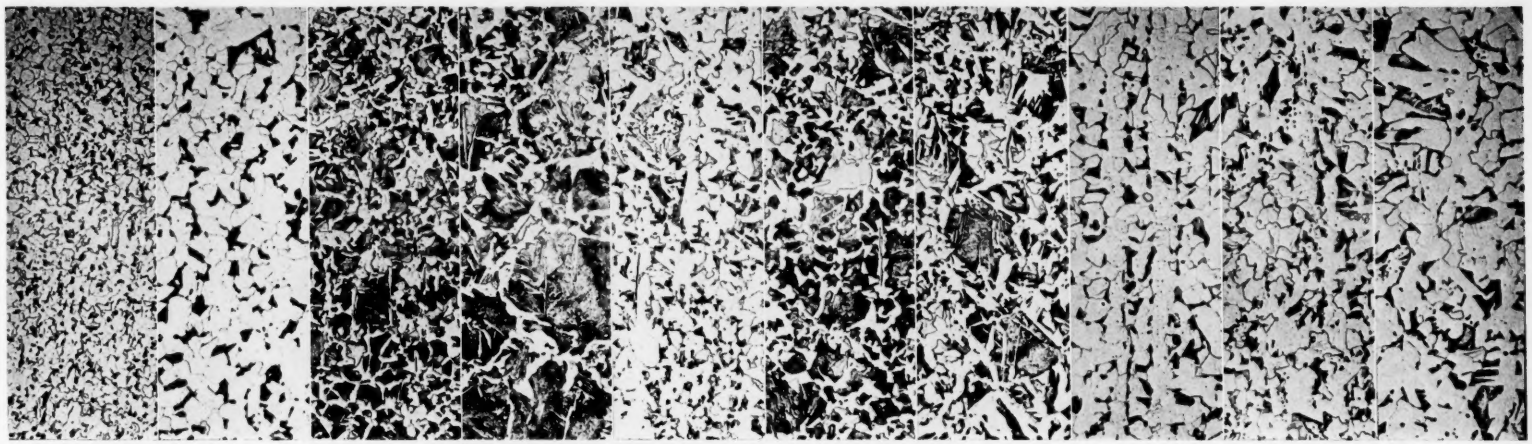


Fig. 2 *a-t*—Normalized steels. The numbers refer to the steel numbers, the normalizing temperatures in °C. (A.C. after 15 min.), and the creep-rate in millionths/hr. at 5 days at 450° C., 8 tons/sq. in. × 150, reduced by $\frac{3}{5}$ linear in reproduction.

(a) (b) (c) (d) (e) (f) (g) (h) (i) (j)

rate in millionths/hr. at 5 days at 450° C., 8 tons/sq. in. × 150, reduced by $\frac{2}{3}$ linear in reproduction.

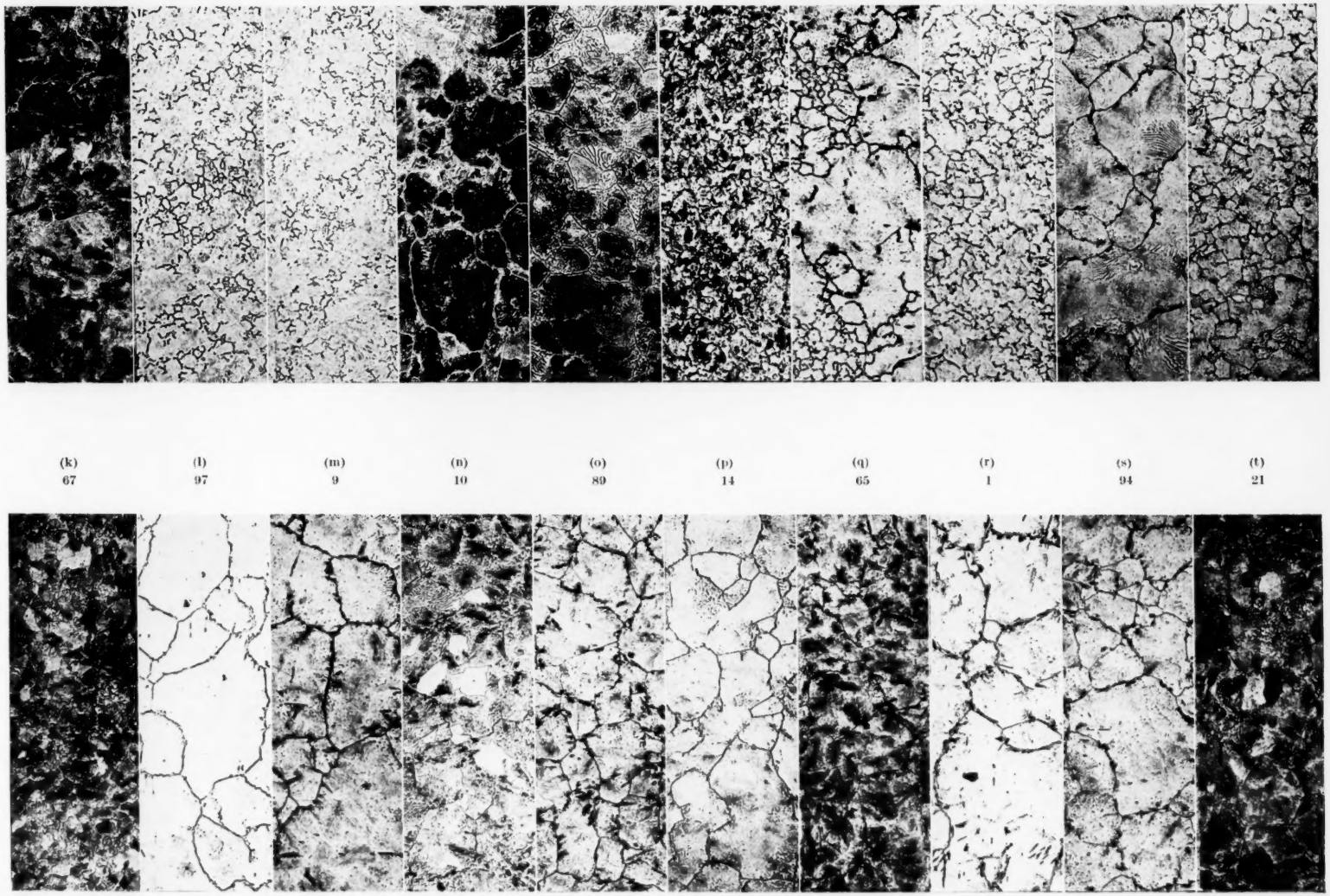


Fig. 3 *a-t*—Steels after McQuaid-Ehn test (8 hr. at 927° C. in carburizing mixture). The numbers given are the steel numbers. × 150 reduced by $\frac{2}{3}$ linear in reproduction.

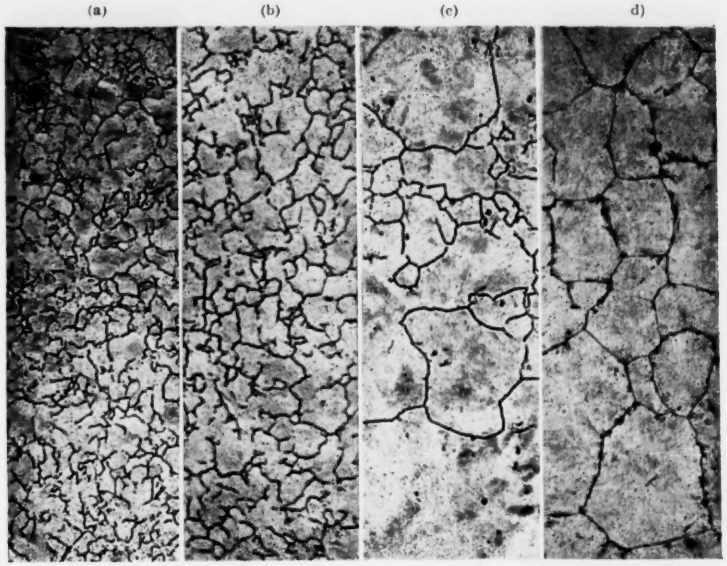


Fig. 4 *a-d*—Effect of further heat-treatment on McQuaid-Ehn specimens x 100

(*a*) Steel 52: 900° C./15 min. S.C.

(*b*) Steel 84: 1100° C./15 min. S.C.

(*c*) Steel 93: 1100° C./15 min. S.C.

(*d*) Steel 94: 1100° C./15 min. S.C.

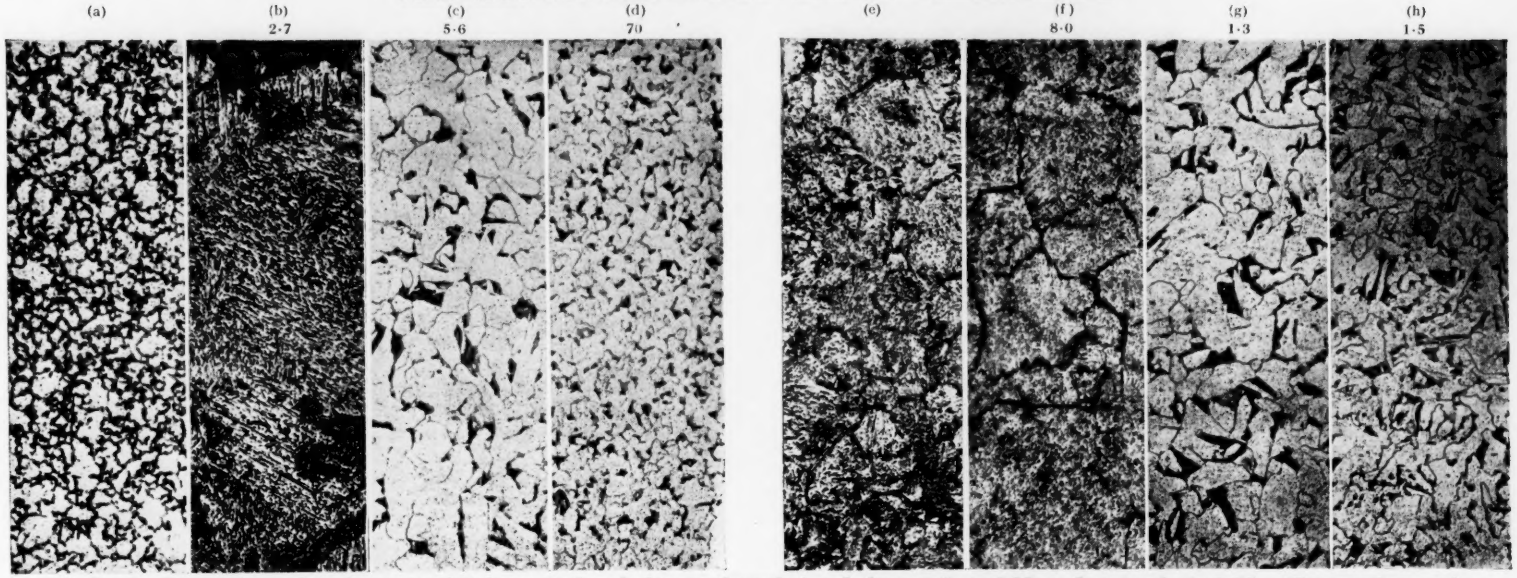


Fig. 5 *a-h*—Comparison of grain coarsening in normal and abnormal steels (*a*—*d* abnormal steel 93, *e*—*h* normal steel 94). The numbers refer to the creep-rates. (*a*) and (*e*) 950° C./15 min. W.Q.; (*b*) and (*f*) 1100° C./15 min. W.Q.; (*c*) and (*g*) 950° C./15 min. A.C. + 1100° C./6 hr. A.C.; (d) and (h) 950° C./15 min. A.C. + 1100° C./6 hr. A.C. + 950° C./15 min. A.C. × 100

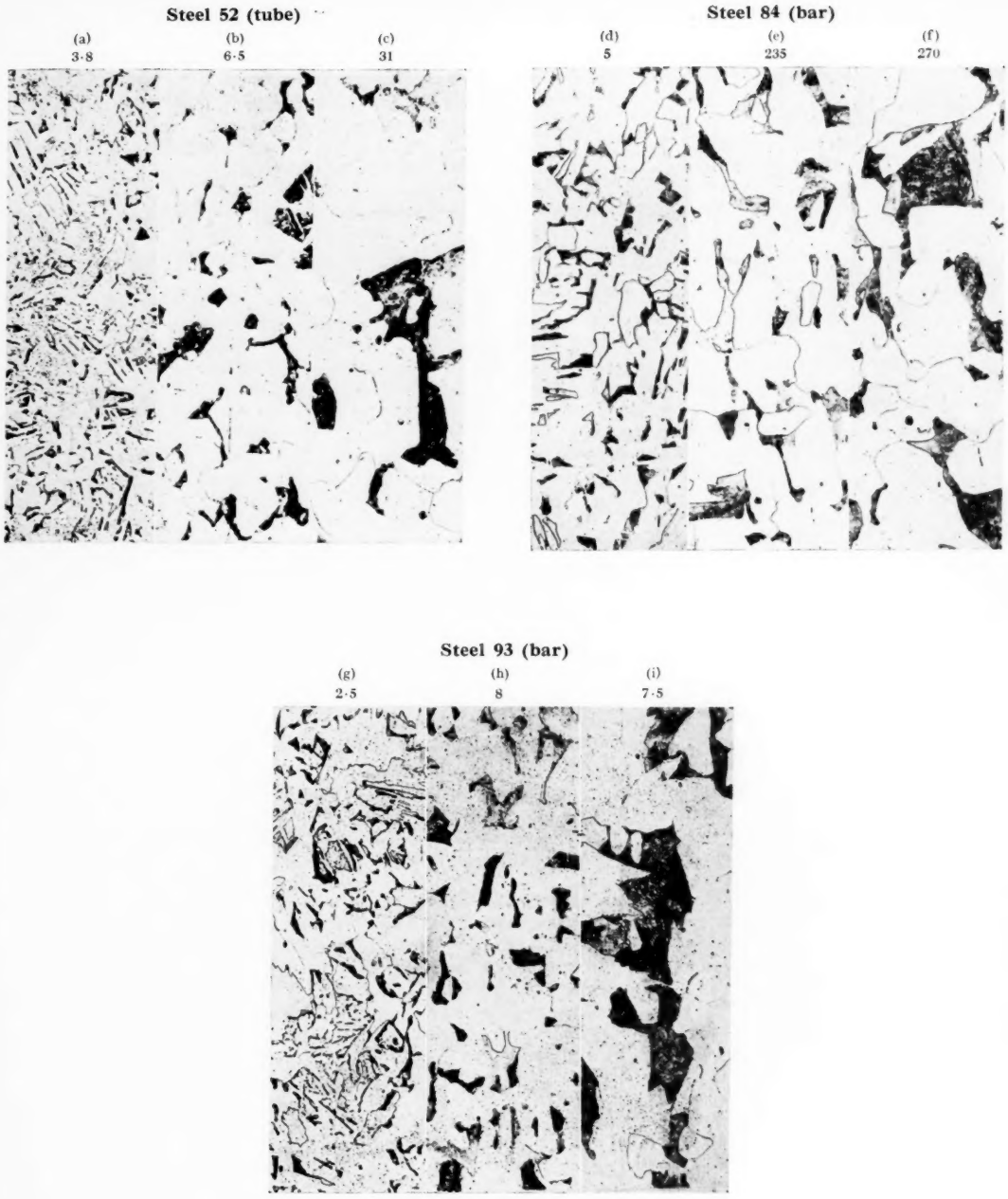


Fig. 6 *a-i*—Effect of rate of cooling from grain-coarsening temperature on abnormal steels. The numbers refer to the creep-rates.

(*a*), (*d*) and (*g*) 1100° C./15 min. A.C. ; (*b*), (*e*) and (*h*) 1100° C./15 min., then slowly cooled to 600° C. in 1·8 hr. ((*b*) 0·65 hr.); (*c*), (*f*) and (*i*) 1100° C./15 min., then slowly cooled to 600° C. in 6 hr. × 100

0·24% of Si without Al being added. The oxygen content of steel 93 is 0·004–0·007% compared with 0·012% in steel 94. There is 0·024% of Al as soluble and 0·010% insoluble in steel 93 compared with $<0·001\%$ soluble and 0·006 insoluble in steel 94. In the McQuaid–Ehn test the former was fine and the latter coarse in grain size. The creep properties of the steels were markedly different, that treated with Al having a creep rate of $6·5 \times 10^{-6}$/hr. as-received and 120×10^{-6}/hr. after normalizing, whereas that treated with Si was of normal creep strength, having a creep rate of $1·0 \times 10^{-6}$/hr. in both conditions.

A comparison of the microstructure of these steels is given in Fig. 5. Comparing Figs. 5*a* and 5*e* the grain size of the quenched (Al-treated) steel was markedly finer in the austenitic condition after similar normalizing from 950° C. After heating a further pair of samples at 1100° C. and then water quenching, the Al-treated steel was now found to be coarser in the austenitic state than its Si-treated counterpart (*cf.* Figs. 5*b* and 5*f* with those of normalized steels in Figs. 2*c* and 2*s*).

After normalizing, followed by coarsening at 1100° C., and slow cooling, the ferrite–pearlite grain sizes of the two samples were as shown in Figs. 5*c* and 5*g*. On the formation of the ferritic pearlite structure there has been considerable refinement of the grain size pre-existing in the austenitic state. The creep rates after coarsening and slow cooling were 5·6 and $1·3 \times 10^{-6}$/hr. for the Al-killed and Si-killed samples respectively. The slow cooling from 1100° C. in 6 hr. did not cause the steels to weaken. Steel 94 had a tendency towards a mixed-grain size, but this was probably due to the persistence of the austenitic grain boundaries in the steel which had a smaller grain size at 1100° C. This mixed-grain size in the ferrite–pearlite structure has been discussed[17] in regard to steel 15.

When, after the coarsening treatment at 1100° C., the steels were normalized, the ferrite–pearlite structure reverted in size to that produced by the original normalizing (compare Figs. 5*d* and 5*h* with Figs. 2*c* and 2*s*). The creep rates of the two samples were then 70 and $1·5 \times 10^{-6}$/hr. for the Al-killed and Si-killed samples respectively.

Steels 88 and 89

These were two acid open-hearth ingots made from the same cast containing 0·26% of Si. An addition of 1 lb. of Al per ton was made to one ingot (88) and no addition to the other. The oxygen content was 0·017% in steel 88 compared with 0·011% in steel 89, although the former has the higher creep-rate. The Al content of steel 88 was also high, 0·010% soluble and 0·012% insoluble compared with 0·001% and $<0·001\%$ for steel 89. The grain sizes of both steels were mixed, but the Al-killed steel showed a greater range; the average size was about the same. This distribution resulted in the smallest grains being found in the Al-killed steel. The untreated steel had creep rates of 2·4 and $2·9 \times 10^{-6}$/hr. in the as-received and normalized conditions respectively, whereas the Al-treated steel had values of 2·0 and 49×10^{-6}/hr. under similar conditions.

COMPARISON OF 23 A.O.H. BOILER-DRUM FORGINGS AND 11 B.O.H. BAR STEELS

The 23 A.O.H. steel forgings for boiler drums had an average creep-rate of $1·5 \times 10^{-6}$/hr. (between 0·5–2·5) after normalizing at 880° C. and tempering at 600° C. with an average McQuaid–Ehn grain size of 2 (from 1–4). These are regarded as high-quality forgings for high-temperature service.

The 11 B.O.H. bar steels, referred to in Table I, have an average creep-rate of $2·45 \times 10^{-6}$/hr. (between 0·4–6·4) in the as-received condition and 14×10^{-6}/hr. (between 2–50) after normalizing. The McQuaid–Ehn size was very variable. The conditions of manufacture of these steels were not individually known, but they were selected at random and not made for high-temperature service. The four steels 64, 72, 67, and 65, given in the tables, were from this batch; it should be noted that the minimum Si content (0·15%) and the minimum Mn content (0·58%) were both high in comparison with the contents of these two elements in the B.O.H. tube and bar steels which had high creep rates.

PROPERTIES OF STEELS GIVEN REPEAT, COARSENING, AND SLOW-COOLING TREATMENTS

Table VII contains the results of tests on 11 materials selected from the abnormal and normal creep steels.

As the creep rate of abnormal steels rose on normalizing, it was considered desirable to re-normalize them to see whether any progressive refinement of the grain size was produced by such heat-treatments. The second normalizing caused some slight decrease in the creep rate in the abnormal steels 52, 84, 93, and 2, but normal steels 10 and 89 remained constant. Steel 94 showed, however, a slightly greater creep-rate.

In column 7 of Table VII the results of three successive treatments—normalizing, coarsening at 1100° C. A.C., and re-normalizing—are given. The abnormal steel 84 shows a marked increase in creep rate by the introduction of intermediate coarsening. Steel 93 was not affected and steel 52 was improved. The seven remaining steels treated by intermediate coarsening showed little change. Column 2 shows that the abnormal steel 88 was improved in creep strength by increasing the normalizing temperature from 910° to 950° C.; this did not apply to the normal steel 89. The improvement caused by higher treatment temperatures, which cause coarsening in the abnormal steels, is shown in column 8, and the weakening effect of lower temperatures in columns 6 and 7 of Table VII. The effect of coarsening after normalizing is to decrease the creep rate (*see* column 5).

A test on steel 93 after coarsening only, which showed a creep rate of $5·6 \times 10^{-6}$/hr. at 8 days at 450° C. under a load of 8 tons/sq. in., was continued for 83 days. The creep rate fell to a minimum of $1·7 \times 10^{-6}$/hr. at 21 days, and rose slightly to 3·2 at the end of the period, showing the permanence of the improvement in this steel. Tests also showed that reduction of the creep rate by treatment at 1100° C. was caused by the mere attainment of this temperature, and that the rate of heating and the time of holding at the temperature had no marked effect on the creep rate.

Table VII

CREEP STRENGTH OF STEELS

Tests at 8 tons/sq. in. at 450° C. at 8 days, millionths/hr.

Effect of Grain Coarsening									Effect of Rate of Cooling from Grain-Coarsening Temp.			
				Normalized + 1100° C. for 6 hr., A.C.					1100° C. for 15 min., then cooled from 1100–600° C.			
Steel No.	Creep Rates of Normalized Steel‡	Normalizing temp., ° C.	Normalized Steel Given Second Normalizing Treatment		15 min. at temp. given below, then A.C.			Lowest Temp. of Rapid Grain Growth, 15 min. Treatment	Air Cooled Rate, 0·08 hr.	0·20–0·37 hr.	0·65–1·8 hr.	6 hr. or longer
					600–800° C.	900–975° C.	1000–1050° C.					
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
52	260	950	202	0·9	...	(950° C.) 90	...	975° C. (very marked growth of a few grains)	3·8	6·5 (0·20 hr.)	6·5 (0·65 hr.)	31 (6 hr.)
84	Bar 240	950	...	...	...	...	...		5	15 (0·37 hr.)	235 (1·8 hr.)	270 (6 hr.)
	Tube 246	950	220	2·2	(600° C.) 24 (700° C.) 52 (800° C.) 490	(910° C.) 430 (950° C.) *510	(1000° C.) 166 (1025° C.) 45 (1050° C.) 28	1025° C. (very marked growth of a few grains)	6	15·5 (0·20 hr.)	185 (0·65 hr.) 580 (1·67 hr.)	620 (10 hr.)
93	120	950	65	5·6 1·7 at 21 days 3·2 at 83 days	(600° C.) 4·6 (700° C.) 52 (800° C.) 130	(900° C.) 154 (950° C.) 70 (975° C.) 47	(1000° C.) 14 (1025° C.) 4·5 (1050° C.) 4·0	975° C. (sudden growth of many grains)	2·5	3·7 (0·37 hr.)	8 (1·8 hr.)	7·5 (6 hr.) 8·0 (12 hr.)
88	49	910	...	...	...	...	...	925° C. (marked growth of a few grains)	...	...	...	3·3 (6 hr.)
	11	950	12	3·7	...	(950° C.) 9	...					
15	16·5	950	...	...	...	(950° C.) 15	...	875° C. (slight growth of many grains)	...	...	12·5† (0·92 hr.)	...
2	18·6	900	6·6	...	...	(900° C.) 9	...	950° C. (marked growth of a few grains)	...	...	7·4† (0·92 hr.)	...
9	4·2	900	...	...	...	(900° C.) 3·7	...	875° C. (slight growth of a few grains)	...	2·5 (0·37 hr.)	4·5† (0·92 hr.)	3·9 (6 hr.)
10	2·0	900	2	...	...	...	...	825° C. (slight growth of a few grains)	...	1·6 (0·37 hr.)	3·5† (0·92 hr.)	2·8 (6 hr.)
89	2·9	910	...	...	...	...	...	No rapid grain growth observed between 875–1000° C.	...	2·5 (0·37 hr.)	...	4·0 (6 hr.)
	2·0	950	2	3·6	...	(950° C.) 2·5	...					
1	1·8	950	...	...	...	(950° C.) 1·9	...	875° C. (slight growth of a few grains)	...	4·5 (0·37 hr.)	2† (0·92 hr.)	6·5 (6 hr.)
94	1·0	950	2·6	1·3	(600° C.) 1·1 (700° C.) 2·1 (800° C.) 1·0	(950° C.) 1·5	...	No rapid grain growth observed between 875–1000° C.	...	2·0 (0·37 hr.)§	...	3·2 (6 hr.)§

* 950° C./15 min. A.C. + 1100° C./6 hr., quenched in fused salt to 950° C., then 950° C./15 min. A.C. gave a creep rate of 1·8 × 10⁻⁴/hr. (if allowed to cool to room temp. after 1100° C. the creep rate would have been 510)
† Preliminary treatment 1100° C./6 hr.
‡ See col. 5 of Table V
§ Previously normalized at 950° C./15 min. A.C.

The effect of cooling the steels rapidly or slowly after coarsening was examined, and the results are given in columns 10–13 of Table VII. The results for the abnormal steel 93 show that the improvement by coarsening was well maintained even after slow cooling for 12 hr.; abnormal steel 52 showed less stability, and steel 84 did not retain the improvement due to coarsening (*see* column 13) and, as shown in column 7, was much weaker than the material given normalizing treatments at 950° C. only.

The microstructures of the three abnormal steels 52, 84, and 93 have been further investigated. Figure 6 shows the appearance of the specimens after treatment. The grain size in the austenitic state at 1100° C. is in all cases coarse, and on air-cooling 1-in. dia. bars a fine ferrite–pearlite structure of low creep-rate is formed. Lengthening the cooling time to 6 hr. causes the ferrite–pearlite structure to coarsen, although it is always finer than the austenitic grain size. In steels 84 and 52 this coarsening of the ferrite–pearlite is accompanied by increased creep-rate. It is usually supposed that a general increase in grain size is accompanied by decreased creep-rate, but in steel 84 the rate does not appear to be controlled by either the original austenitic grain size or the ferrite–pearlite structure.

Treatment of normal steels at 1100° C. had little effect on the creep rate, and slow cooling from 1100° C. for 6 hr. on five of the normal steels caused a slight increase in the creep rate. The general stability of the normal steels after heat-treatment is characteristic of their general behaviour.

After coarsening at 1100° C. the grain size of normal and abnormal steels is not greatly different, the former beginning grain growth at a lower temperature than the latter, 850° C. or below instead of 975° C. or above, and showing growth over a longer temperature range. The abnormal steels appear to have a characteristically delayed grain growth on reheating, but when individual grains begin to grow, large crystals are soon evident, and the finer grains are slowly absorbed. While this is going on the creep rate of the steels is improving. Column 9 in Table VII refers to the changes on reheating various steels to various temperatures and recording the structures.

This subject has been considered elsewhere in detail,[1] and the austenitic grain size and the resulting ferrite–pearlite grain sizes after normalizing are given for every 25° C. throughout grain growth. An exhaustive investigation was made into the relation between the size of the individual ferrite and pearlite grains in these steels and their creep rates. Appropriate methods of measuring these grain sizes were developed and are described in detail. A general relationship was found between the ferrite or pearlite grain size and the creep rate. The maximum ferrite and pearlite grain size was determined by the austenitic grain size. A fine ferrite and pearlite grain size was produced from a fine-grained austenite, and consequently was often associated with high creep-rate in the normalized condition. On the other hand a fine ferrite and pearlite structure produced from a coarse austenite, *e.g.*, by rapid cooling, could be associated with a low creep-rate. Coarse ferrite and pearlite structures could also be associated with high creep-rate, *e.g.*, when certain abnormal steels were cooled through the critical range very slowly, whereas most steels of low creep-rate have moderately coarse ferrite and pearlite structures.

EFFECT OF SPHEROIDIZATION AND GRAPHITIZATION ON WROUGHT STEELS

Heat-treatment of the steels at 650° C. causes the lamellar pearlite to spheroidize, accompanied by a marked increase in the creep rate of samples of both normal and abnormal steels.

Bailey and Roberts[12] showed that the ratio of the spheroidization rate at 650° C. to that at 450° C. was about 20,000 : 1. Under the standard condition of testing, the normal steel 94 in the normalized condition showed a creep rate of 1×10^{-6}/hr. Eight hours' spheroidization at 650° C. did not increase the creep rate to $> 1{\cdot}2\text{–}3{\cdot}0 \times 10^{-6}$/hr. This spheroidizing treatment is equivalent to $>$ 150,000 hr. at the service temperature of 450° C., but lengthening the spheroidization time to 24 hr. at 650° C. reduced the creep resistance of three samples, the rates then being $10{\cdot}5$, $32{\cdot}5$, and 34×10^{-6}/hr. These values are still within the requirements of certain B.S.I. specifications.

When this steel was given a heat-treatment at 1100° C. for 15 min., the creep rate was $1{\cdot}3 \times 10^{-6}$/hr., slightly lower than in the normalized condition after 950° C. Two specimens previously treated at 1100° and 950° C. were heavily spheroidized by 60 days' heating at 650° C. The sample treated at the higher temperature had a higher creep-rate than that treated at the lower temperature, *viz.*, 237 compared with 90×10^{-6}/hr., which was unexpected in view of the improved creep-rate of an abnormal steel when heat-treated at 1100° C. A chemical analysis of the normal steel after treatment at 1100° C. and spheroidization showed that its carbon and oxygen contents had not changed during treatment, and therefore the effect noted above was not due to a change of composition.

A normalized sample of the abnormal steel 93 with a creep rate of 120×10^{-6}/hr. was treated at 1100° C. for 15 min. and air-cooled, causing the creep rate to improve to $2{\cdot}5 \times 10^{-6}$/hr. The steel was then spheroidized by a 60-day treatment at 650° C., and the creep rate became 338×10^{-6}/hr. The creep strengths of the highly abnormal steel 93 and the normal steel 94, with a comparable creep rate of 237, can thus be made reasonably similar by this very heavy spheroidizing treatment at 650° C. The Si and Mn contents of these steels are markedly different, and although they were so dissimilar in creep strength in the normalized condition, they were more alike in the hot-rolled state, the creep rates being $6{\cdot}5$ and $1{\cdot}0 \times 10^{-6}$/hr. respectively.

A sample of a 7-in. steam-conveying pipe after 54,000 hr. service at 430° C. spread over 10 years was appreciably spheroidized, and showed a creep rate under the standard test conditions of between 120–180×10^{-6}/hr. After re-normalizing the creep rate improved to 6–8×10^{-6}/hr., which is probably close to the rate at the beginning of service, assuming that the steel has been originally normalized.

The deterioration in creep strength of three unused

Table VIII

CREEP RATE OF CAST AND WROUGHT STEELS

8 tons/sq. in. at 450° C. at 8 days

Steel No.	Creep Rate As Cast, millionths/hr.	Cast and Annealed		Normalized Rolled Bar	
		Creep Rates, millionths/hr.	Annealing Treatment	Creep Rates, millionths/hr.	Normalizing Treatment
93	143 (sand cast)*	115	6 hr. at 975° C.*	120	15 min. at 950° C.
88	37 (ingot)	40	15 min. at 910° C.	49	15 min. at 910° C.
89	2·9 (ingot)	4	15 min. at 910° C.	2·9	15 min. at 910° C.
94	8·5 (sand cast)*	0·67	6 hr. at 975° C.*	1·0	15 min. at 950° C.

* Creep rate determined at the end of 15 days

materials in the form of a steam pipe, a superheater header and a superheater tube (steels 35, 75, and 52 respectively) was examined after 12 hr. spheroidization at 650° C. In tests lasting for 200 hr. at 5 tons/sq. in. at 460° C. the estimated creep-rate increased in the case of the steam pipe from 7–21 $\times$ 10^{-6}/hr., in the superheater header from 4·5–9 $\times$ 10^{-6}/hr. and in the superheater tube from 6·5–33 $\times$ 10^{-6}/hr. The superheater header was an acid open-hearth steel, whereas the steam pipe and the superheater tube were made by the basic open-hearth process.

Either the steam-conveying pipe underwent more damage in service by overheating, etc., than is indicated by the accelerated spheroidization of 12 hr. at 650° C., or the steel spheroidizes more rapidly than the steam-pipe steel.

Graphitization takes place in carbon steels after appreciable spheroidization, and not in the periods of creep testing up to 20 days given to the steels described in this paper. A general account of the development of graphitization has been published,[11] and reference has been made to some of the steels described in this paper (*see* column 3 of Table I).

COMPARISON OF CAST AND WROUGHT STEELS

Specimens of two abnormally high creep-rate steels and of two normal steels were examined in the cast, cast-annealed, and wrought states and the results are given in Table VIII.

These tests show that working the cast material does not affect the inherent creep resistance of these steels.

STEELS IN THE HARDENED AND TEMPERED STATE

Comparative creep tests were made to find out whether these steels of widely different creep-rates could be improved by oil quenching and tempering. The results, in Table IX, show that steel 93, which had an abnormally high creep-rate in the normalized condition, was greatly strengthened by oil quenching. Tempering for 5 min. at 650° C. caused a return to the strength shown by the normalized specimen. Further tempering for a total time of 60 min. increased the creep rate to 245 $\times$ 10^{-6}/hr.

Steel 97, which was moderately strong, was slightly improved by hardening and tempering for 1 hr. at 650° C., whereas steel 94, which had a good creep strength in the normalized state, was not greatly altered by similar hardening and tempering.

CONCLUSIONS

The present work considers the general creep and grain-size behaviour of several types of carbon steel with a wide range of creep rates. The steels with abnormally high creep-rates are of peculiar interest although not on the whole suitable for high-temperature applications. The methods of manufacture, particularly in regard to the deoxidation of the molten steels, are considered in relation to the subsequent creep and grain-size behaviour. Steels of low or normal creep-rate can be produced under readily reproducible conditions, and steels of high creep-rate can be produced by using appropriate but different melting and deoxidizing conditions. Acid open-hearth steels show consistently good creep-properties, and may thus be preferred for prolonged service at high temperatures. Under carefully controlled conditions, basic open-hearth steels can be produced of equal creep strength. Large additions of Al may produce steels with high creep-rates. A low oxygen content in B.O.H. steels is probably indicative of the use of this reducing agent. Probably 0·5 lb. of Al per ton should not be exceeded if a creep rate of $< 2 \times 10^{-6}$/hr. under 8 tons/sq. in. at 450° C. is consistently required. If the manufacturing conditions are well controlled, additions of even 1·5 lb. of Al per ton can be given without the creep rate exceeding 50 $\times$ 10^{-6}/hr. at the end of a two-day test. It is desirable, however, to have a Si content of about 0·13% with $\lessapprox$ 0·60% of Mn.

The high creep-rate of certain normalized steels was traced back to the ingot state, but the coarsening of

Table IX

CREEP TESTS ON STEELS 93, 97, AND 94

Creep rate after 20 days under 8 tons/sq. in. at 450° C., millionths/hr.

Condition As Tested	Steel 93	Steel 97	Steel 94
Normalized from 950° C./15 min.	107	10	0·4
Oil-quenched from 950° C./15 min.	30	...	...
950° C., O.Q. + T. 650° C./5 min.	102	...	...
950° C., O.Q. + T. 650° C./60 min.	245	3	0·65

grain size in these steels by treatment at 1100° C. gives good creep properties. Certain highly abnormal steels do not retain this improvement if cooled very slowly.

Long-time creep resistance at 450° C. is not improved by an increase in carbon content to 0·40%, although the addition of carbon improves the ultimate tensile strength.

Austenitic and McQuaid–Ehn grain size and the ferrite–pearlite grain size of normalized and slowly cooled samples indicate possible creep characteristics, but there are some marked exceptions to the general rule that a coarser grain-size gives a material more resistant to creep. A sudden increase in grain size in the region of 1000° C. on reheating a steel is a good indication that a steel has a high creep-rate when normalized from 900–950° C. The McQuaid–Ehn test can indicate steels of high creep-rate, but fails to distinguish between good and moderately good steels.

Steels of normal creep-rate maintain their good creep properties after a wide range of heat-treatments, but not after spheroidizing treatments. The greater resistance to spheroidization shown by normal steels in comparison with abnormal steels means less weakening in creep resistance during service. There is no advantage in treating normal steels at 1100° C.

If heat-treatments at high temperatures of 1050–1100° C. were given to high creep-rate steels, a marked improvement in creep strength would be produced. On the other hand, during service in a power plant, these steels should not be allowed to attain a temperature at which rapid spheroidization occurs, as the strengthening imparted by such treatments would not be retained.

Although some fine-grained steels were found to have abnormally high creep-rates at 450° C., and were obviously unsuitable for service at this temperature, they would be suitable at lower temperatures.

It is suggested that the difference in creep behaviour between high and low creep-rate steels is due to the respective presence or absence of a constituent which causes nucleation of the carbide on cooling the austenite through the critical range; the nucleating constituent is probably an aluminium carbide or nitride which is insoluble in the ferrite and fully soluble in austenite at 1100° C., but only feebly so at 950° C. On reheating steels containing the separated nucleating constituent, the grain growth is delayed until the constituent has been taken into solid solution.

Acknowledgments

This work was carried out by the Metallurgy and Engineering Divisions of the National Physical Laboratory. Many persons were associated with various aspects of the work, and particular acknowledgment is made to Dr. A. E. Johnson, Mr. T. H. Schofield, and Dr. M. L. Becker. This paper is published by permission of the Director of the Laboratory.

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Some Effects of Order–Disorder in Iron–Aluminium Alloys

By W. D. Bennett, B.Sc., Ph.D.

SYNOPSIS

The magnetic and electrical properties of the superlattice region Fe_3Al in a series of iron–aluminium alloys have been investigated.

Some anomalous variations in electrical resistance and in magnetic coercive force near the precipitous order–disorder change (450–560° C.) were examined in an apparatus able to work *in vacuo* at high temperatures. The resistivity is abnormally high in this region; from theoretical considerations a fall in resistivity would be expected on cooling at the critical temperature of order–disorder. The difference between theory and experiment can be accounted for by the presence of antiphase nuclei. Values of resistivity for quenched and annealed alloys at room temperature lie on curves which are in agreement with the ordering process suggested by Bradley and Jay.

It is possible to account for changes in coercive force on the Becker 'stress' theory of magnetization. The presence of mixed regions of order and disorder gives rise to an internal stress distribution in the region of 500° C., which partly explains the relatively large increase in coercive force.

THE object of this research was to determine the influence of varying degrees of order on the magnetic and electrical properties of an alloy. The superlattice Fe_3Al was used because it is magnetic, has a high electrical resistivity, and can readily be ordered or disordered by heat-treatment.

PREPARATION OF ALLOY SPECIMENS

When investigating *B–H* properties at low magnetic field strengths, it is essential to have alloys free from impurities because the latter will produce, on heat-treatment, stresses which will be confused with any effects due to order–disorder; 99·998% pure aluminium and spectrographically pure iron were therefore used. Melts of 200-g. weight were made in a H.F. vacuum furnace, using a pure alumina cylindrical crucible, moulded with a fair amount of precision, in which the melts were allowed to solidify.

To promote homogeneity, a vacuum annealing furnace was used in which the alloy was annealed at 1250° C. for 18 hr. After all machining processes or any cold-working, the alloy was annealed at 700° C. for 3 hr.; this was found to be sufficient to remove the effects of cold-work.

From the solid cylindrical-shaped melt the largest hollow cylinder possible was cut, with $\frac{1}{8}$-in. walls. The cylinder had to be free from all wall impurities and blow-holes, and was usually 1 in. long with an internal diameter of 1 in.; it was used for high-temperature *B–H* measurements. This specimen could also be used for room-temperature magnetic measurements, but a $\frac{1}{8}$-in. slice (giving an anchor-ring type specimen) was found to be more convenient. A $\frac{1}{16}$-in. slice cut from the cylinder, with a gap, served as an electrical resistance specimen (*see* Fig. 1).

X-RAY EVIDENCE

Powder samples from all the alloys used were heat-treated in vacuum-sealed quartz tubes and used in a Debye-Scherrer X-ray camera. The results were in close agreement with those obtained by Bradley and Jay[1, 2] for a body-centred structure (Miller indices 2, 4, 6, 8, etc.); lattice parameters agreed to four figures.

An interesting but rather disturbing addition, on films for alloys which showed body-centred superlattice lines in the annealed condition, was the presence of a definite but rather faint set of lines characteristic of a face-centred lattice. These lines appeared for both quenched and annealed alloys. At first they were thought to be spurious, and careful checks were made using the specimen holder without powder and with pure iron powder; no face-centred lines appeared. Alloys from entirely different sources of manufacture showed similar results.

It was not possible to detect the face-centred structure under the microscope, using suitable etching agents. Photomicrographs showed only one phase, together with some very small hard particles, probably caused by some trace of a third element. These particles occurred only in odd patches, and certainly would not amount to more than 1% of the total weight of metal—a quantity too small to account for the additional X-ray lines. The microscope showed the metals to be quite sound, except for an occasional area of porosity.

These results suggest that the face-centred phase occurs only in the powder form; it may be attributed to silicon contamination of the alloy precipitating a second phase in the order–disorder region.

EXPERIMENTAL ARRANGEMENT

Magnetic measurements of the *B–H* properties of the alloy were carried out using the standard ballistic method. In this method the specimen, in the form of an anchor ring or cylinder, is wound with primary and secondary coils. A measured current in the

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primary of the specimen is proportional to the magnetic field H. The secondary is in series with a ballistic galvanometer and the secondary of a standard mutual inductance. By reversing the current in the specimen primary a ballistic deflection is produced on the galvanometer, proportional to the magnetic induction B. By modifying the simple reversing circuit to switch from a given positive value of field to a variable negative one, it is possible to cover the complete hysteresis loop. The galvanometer deflection is calibrated by reversing a measured current in the primary of the mutual inductance. For room-temperature measurements the primary and secondary windings are wound one on top of the other, with insulation tape on the core and between the two windings.

High-temperature measurements of electrical resistance and B–H properties were made using the same vacuum furnace with interchangeable water jackets (Fig. 1 shows the arrangement for resistance measurements). The furnace was temperature-controlled by means of an electronic controller working in conjunction with a platinum resistance thermometer and vacuum relay switch. The controller (developed at the B.S.A. Group Research Centre, Sheffield) used a modified Prosser circuit with a number of refinements added. The temperature could be controlled to within $\pm \frac{1}{2}$° C. over any period of time, with a much smaller variation over short periods of about 1 hr. Slow cooling was effected by driving the potentiometer wire (in the bridge circuit of the temperature controller) through a high-ratio gear mechanism.

The measurement of B–H properties up to 700° C. presented two major problems : obtaining the necessary electrical insulation between the specimen and the primary and secondary coils, and obtaining a circuit sensitivity high enough to measure the low values of induction occurring at high temperatures. To produce good insulation it was necessary to use thin quartz cylinders to line the cylindrical specimen on the inner and outer surfaces. Primary and secondary coils were wound on opposite halves of the ring with 60–70 turns each of 20 and 30 S.W.G. asbestos-covered wire, respectively. On heating *in vacuo*, a thin layer of carbon was produced on the quartz by the wax in the asbestos. To overcome this the specimen, with primary and secondary coils in position, was heated up to 800° C. in air for 3–4 min. before it was inserted in the vacuum furnace. For both magnetic and electrical properties the temperature was measured by a Pt/Pt–Rh thermocouple in contact with the specimen.

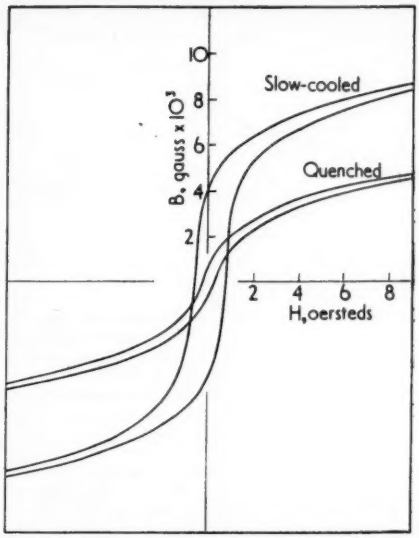
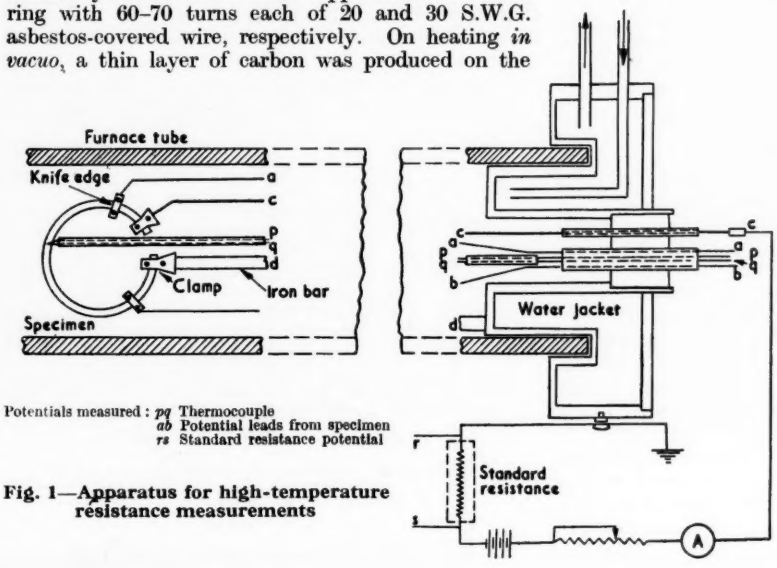


Fig. 2—Typical B–H curves for a quenched and annealed alloy (24 at.-% Al)

For the measurement of electrical resistance at high temperatures, a $\frac{1}{16}$-in. slice was cut, with a gap, from the magnetic cylindrical specimens, a current of $\frac{1}{2}$ amp. was passed through the specimen, and the potential across the knife edges was measured on a potentiometer (*see* Fig. 1). The potential across a standard resistance in series with the specimen gave the value of the current. After the first few results had been taken it was found necessary to replace the knife edges and current lead clamps by spot welding. This gave much greater reliability at the higher temperatures. No attempt was made to obtain absolute values of resistivity, although a value to within 1% could be obtained by carefully measuring the distance between the knife edges.



Potentials measured : *pq* Thermocouple
ab Potential leads from specimen
rs Standard resistance potential

Fig. 1—Apparatus for high-temperature resistance measurements

RESULTS

At Room Temperature

The first series of results was taken at room temperature on alloys which had been quenched and

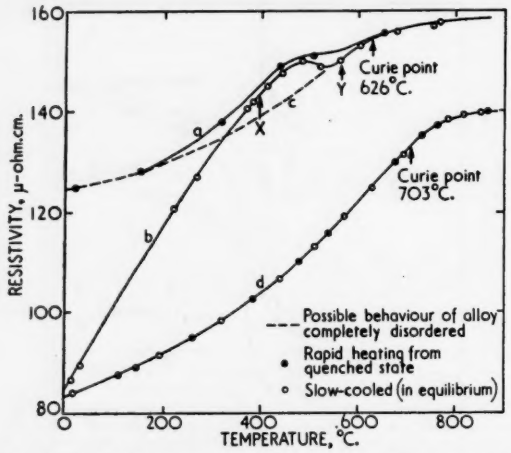


Fig. 3—Resistivity/temperature curves. Curves *a*, *b*, and *c* are for alloy No. 8 (23·7% Al); curve *d* is for alloy No. 12 (17·6% Al)

annealed, annealing being done by slow cooling at a series of constant rates (50, 20, 10, 5, and 1° C. per hour) from 700° C. Work by Bradley and Jay[1, 2] indicates that alloys which have been so treated will be disordered and ordered, respectively. Resistance measurements confirmed this, the resistance increasing by as much as 50% on quenching the annealed alloy of Fe_3Al. Magnetic measurements were not so decisive; although considerable changes took place in the shape of the *B–H* curves, some of these changes might well be attributed to the setting up of internal stresses on quenching. The presence of such stresses was illustrated by one ring which cracked on quenching, producing a gap 2 mm. wide. Typical *B–H* curves for quenched and annealed alloys are illustrated in Fig. 2; the main effects of quenching are to reduce the coercivity and the hysteresis loss.

To overcome the undesirable effects of these stresses it was decided to carry out experiments at different temperatures, the alloy being annealed after slow cooling from 700° C. In this way it was possible to produce various states of order, the order being directly related to the temperature.

Resistivity at Higher Temperatures

Curve *a* of Fig. 3 shows the typical behaviour of an Fe_3Al slow-cooled alloy when heated at about 10° C./min. Curve *b* is a graph of the equilibrium positions (*i.e.*, of the steady values of resistivity at given temperatures); it shows a change in curvature at the Curie point, 626° C., and in the region 400–560° C. For slower rates of heating, curve *a* became more concave, running into the equilibrium curve at a much lower temperature.

Curve *d*, for a 17·6 at.-% Al alloy, shows only the change in curvature at the Curie point and no obvious change due to order–disorder. From X-ray intensity measurements, Bradley and Jay[2] have already shown (*loc. cit.*, Fig. 5) that no ordering is expected in this alloy. Thus curve *d* shows the behaviour of an F_3Al alloy completely disordered at all temperatures, and a curve of this type can be fitted to curve *a* for the 23·5% Al alloy. The resistivities of the disordered alloy at room temperature and above 560° C. are known, and curve *c* shows the possible resistivity/temperature curve for the disordered alloy. The resistance is increased by the initial stages of ordering in the quenched alloy.

This rather unexpected result is confirmed by the shape of the equilibrium curve, which instead of showing a steep drop at the temperature of 540° C., as would be expected from the sudden onset of order at the critical temperature, appears to flatten off and even shows a slight rise.

It will be noticed that the change in curvature starts at a temperature between 540° and 560° C., the critical temperature range, and finishes at a temperature between 380° and 400° C., where the curve becomes almost a straight line. These changes are shown at *Y* and *X*, respectively, on Fig. 3. Reference to theoretical order/temperature curves[3, 4] shows that this region corresponds to the temperature range for precipitous ordering or disordering.

An explanation of this apparent increase in resistivity on ordering is to be found in a modification of Sykes' idea of antiphase nuclei.[5, 6] When ordering is started on cooling, it builds up in separate nuclei, which are at first very small, independent of each other, and separated by disordered alloy. This ordering, which is a tendency for aluminium atoms to go to definite α sites in the lattice, can take place by the aluminium going either to positions *B* or to positions *D* in Fig. 4, and the fact that the nuclei will be ordering indiscriminately in two different ways means that they will be out of phase. As the temperature decreases, the size of these nuclei will increase with increasing order; but so long as they are out of phase there will be zero long-distance order *S* and hence no fall in the resistivity. In fact, there may be an increase in resistance, owing to the boundary effect between nuclei, the setting up of local stresses, and the possible segregation of small impurities in this region. When these nuclei build up to adjacent domains of order, an ordering effect at the boundary will creep through the alloy, producing one continuous region of order with no out-of-phase regions. Once this process has started there will be a preponderance of one type of order; hence there will be a measure

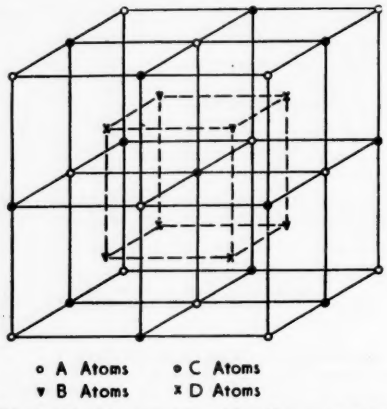


Fig. 4—Fe_3Al structure (Bradley and Jay[2])

of long-distance order, which will start a decrease in resistance. The process is reversible, since an increase in temperature will produce small out-of-phase domains which will increase in size with increasing temperature and decreasing inherent order.

A first objection to this explanation is that the thermal energy will be insufficient to remove the boundary between antiphase nuclei. This is not so, however, if the operation only involves the movement of B and D atoms (Fig. 4); the nuclei will be small, and the temperature will be high enough to promote order from disorder and therefore sufficient to exchange pairs of atoms in B and D positions, giving a lower configurational energy. The ease with which one nucleus can be absorbed by another explains the short relaxation time of ordering in this alloy.

Curve c of Fig. 5 is the resistivity/temperature curve for a 21·5% Al alloy (No. 15). The break away from the main curve d occurs at X, a temperature of 500° C., which corresponds to the critical temperature for this alloy and is lower than that for alloy No. 8, owing to the fall in the configurational energy E_0. The Bragg-Williams[3] theory gives a critical temperature

$$T_c = \frac{V_0}{4k} = \frac{2E_0}{Nk},$$

where V_0 = energy required to 'disorder' an ordered pair of 'unlike' atoms
E_0 = entire order – disorder transformation energy
N = number of atomic sites
k = Boltzmann's universal gas content.

Similar graphs for alloy No. 16 (26·9% Al) are shown in curves a and b, but here the Curie point has been lowered to within the range of maximum order–disorder activity, thus screening any changes taking place at the critical temperature.

Curves a and b in Fig. 6 are for alloys of compositions 24·5% and 25·8% Al, respectively. There appears to be no marked difference in their shape, apart from that due to the difference in Curie point, and they both have the same characteristic maximum at about 480° C.

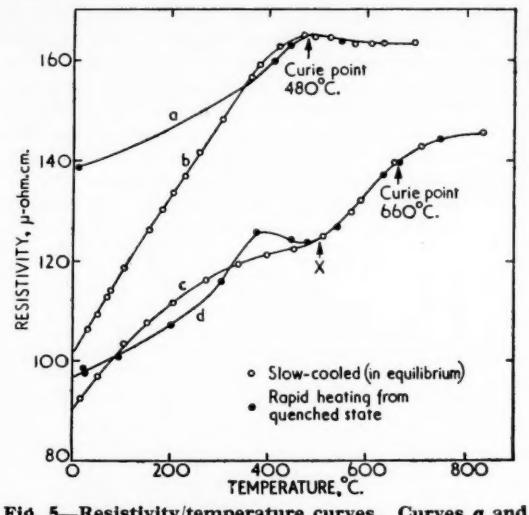


Fig. 5—Resistivity/temperature curves. Curves a and b are for alloy No. 16 (26·9% Al); curves c and d are for alloy No. 15 (21·5% Al)

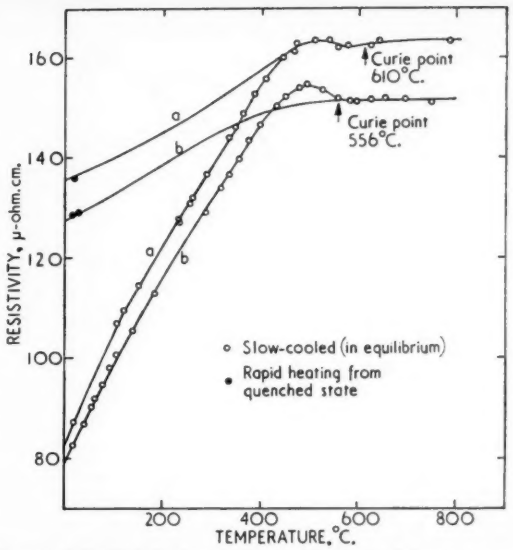


Fig. 6—Resistivity/temperature curves. Curves a are for alloy No. 14 (24·5% Al); curves b are for alloy No. 13 (25·8% Al)

The lower temperature range was investigated more closely for alloys Nos. 13, 14, and 16 (Figs. 5 and 6). There is a definite, but very small, change in gradient in the equilibrium curves at a temperature between 100° and 110° C., which is rather difficult to explain but may be caused by some small impurity.

One important feature common to all these curves is the large difference between the gradients $d\rho/dT$ of the equilibrium curve and the curve for a disordered alloy. According to the quantum theory of conductivity, this is another indication of the presence of antiphase nuclei.

The quantum theory of conductivity gives a simple explanation of the high resistance of alloys. An electron moving in a perfect lattice does so quite freely, which means that such a lattice has zero resistance; the resistance of a pure metal is due to the thermal agitation of the atoms, which destroys the periodicity of the lattice. This periodicity of the field within the lattice may also be broken by the introduction of a foreign atom, which may deflect electrons and so give rise to a resistance even at absolute zero, when there is no thermal agitation.

The resistivity ρ of a metal may be written:

$$\rho = \frac{m}{Ne^2} \cdot \frac{1}{\tau}$$

where N is the effective number of electrons per unit volume and $1/\tau$ is the number of times per second that an electron is deflected.

If $1/\tau_0$ is the number of times per second that an electron is deflected by a foreign atom, and if $1/\tau_T$ is the number of times that the electron is deflected as a result of thermal oscillation of the atoms, then:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_T}.$$

The resistivity of the alloy may therefore be written:

$$\rho = \rho_0 + \rho_T$$

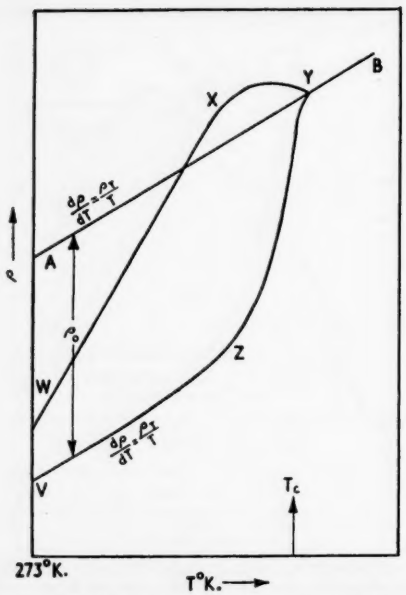


Fig. 7—Resistivity/temperature curves predicted by theory, for ordered and disordered alloys

where $\rho_0 = \frac{m}{Ne^2} \cdot \frac{1}{\tau_0}$ and $\rho_T = \frac{m}{Ne^2} \cdot \frac{1}{\tau_T}$. The term ρ_0 is the resistance at absolute zero and is independent of temperature; ρ_T is approximately proportional to temperature, as for a pure metal.

The gradient of a resistivity/temperature curve is $d\rho/dT$, where $d\rho/dT = d\rho_0/dT = d\rho_T/dT$. For an ordered alloy, $d\rho_0/dT = 0$, since $\rho_0 = 0$ at all temperatures. Therefore $d\rho/dT = d\rho_T/dT \simeq \rho_T/T$. For a disordered alloy, $\rho_0 =$ constant (at all temperatures if the alloy is heated rapidly from the quenched state, allowing insufficient time to order below the critical temperature); therefore $d\rho/dT = d\rho_T/dT \simeq \rho_T/T$. The gradients of resistivity/temperature graphs should thus be the same for ordered and disordered alloys. Figure 7 illustrates the type of curve predicted by the above treatment. The portion AYB for the disordered alloy is in rough agreement with experiment. The equilibrium curve $BYZV$, however, is very different from the corresponding experimental curve $BYXW$, and this may be explained by the presence of antiphase nuclei, which decrease the long-range order and increase the resistance. The steep gradient of WX may then be attributed to one phase of order increasing, in relation to the other, with decreasing temperature.

Theoretically, the equilibrium curve, when extrapolated to absolute zero, should give zero resistance, but the experimental curves for the two alloys nearest to the Fe_3Al composition (Nos. 13 and 14) give a value of 20 μ-ohm.cm. This may be because the growth of the predominant phase is too slow to give single-phase order at absolute zero.

Magnetic Results

A typical set of hysteresis loops is shown in Fig. 8. At each temperature the specimen was annealed for some hours, until no further changes in the shape or

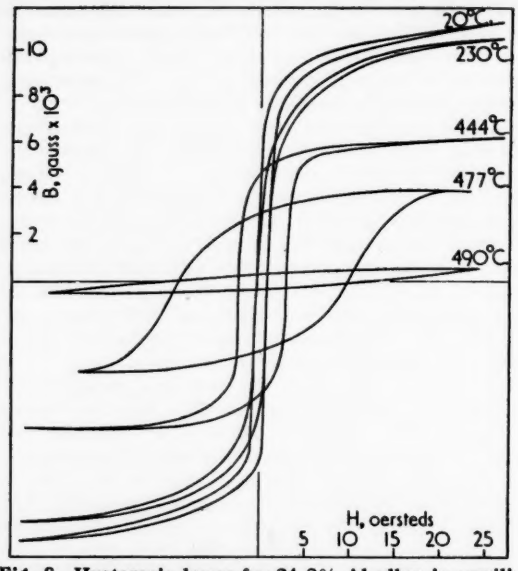


Fig. 8—Hysteresis loops for 24·2% Al alloy in equilibrium at different temperatures

size of the hysteresis loop were noticed. The alloy in this state will be referred to as being in equilibrium. At temperatures up to 450° C. the time to reach equilibrium was not measurable, but between 450° and 500° C. it was appreciable—at 477° C., two days were required.

Up to 400° C. no big changes took place in the shape of the hysteresis loop. From 400° to 500° C., however, there was a steady increase in the width of the loop, the change being mainly in coercivity. Above 500° C. and approaching the Curie point the coercivity fell rapidly to zero; this was, of course, inevitable as the alloy became non-magnetic. The hysteresis loops within the latter range are not shown on the diagram, because of their very small scale.

The whole change in coercivity is summed up in Fig. 9, which is a graph of coercive force plotted against temperature for alloy No. 8 (23·7% Al). Just below the Curie point there is a steep drop in coercivity, and it is this part of the curve which is most difficult to record. The curve shows that to record points with accuracy in this region it is necessary to have the temperature controlled to within at least $\pm \frac{1}{2}$° C. This was not always possible, owing to the heating

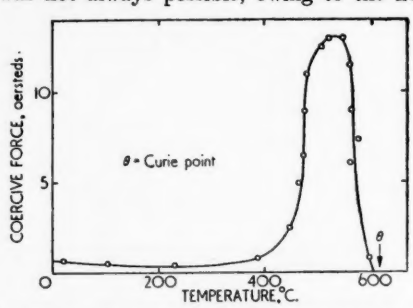


Fig. 9—Coercive-force/temperature curve for 23·7% Al alloy No. 8

effect of the current in the primary H coil, which was not immediately corrected for by the temperature controller. This heating effect was reduced to a minimum by carefully selecting the gauge of wire and using a minimum field H (although the latter had to be at least twice the coercive force), and also by cutting down the number of readings to the few necessary for measuring coercive force alone. With this in mind it was decided not to study the changes in the complete hysteresis loop, but to confine the investigations to a study of changes in coercive force, which appeared to be the parameter most closely affected by the order–disorder changes.

The first investigations, in a series of this type of measurement, were on the coercive force of iron at high temperatures, to see if there was any anomalous behaviour in the region 400–500° C. From curve *a* of Fig. 10*a* it can be seen that the change in curvature that does take place is only slight and not in this temperature region.

Other measurements were carried out on the same alloys used for resistivity measurements ; these alloys had been made with spectrographic iron. Curve *b* of Fig. 10*a* is of particular interest in that it shows a slight ' peak ' effect for an alloy that has no order–disorder properties according to resistivity measurements (*see* Fig. 3) but may contain nuclei of short-range order, which would not show up as superlattice lines or as changes in resistivity. The results suggest that the increase in coercive force is connected with the breaking up of these nuclei.

Comparison of Figs. 9 and 3 shows that the increase in coercive force occurs in the same temperature range XY as does the change in resistivity. With increasing temperature, X corresponds to the temperature at which the antiphase nuclei are in equal numbers and adjacent to each other. A further increase in temperatures will tend to form ' islands ' of ordered antiphase nuclei in a disordered lattice. This may be part of the mechanism producing the high coercive force.

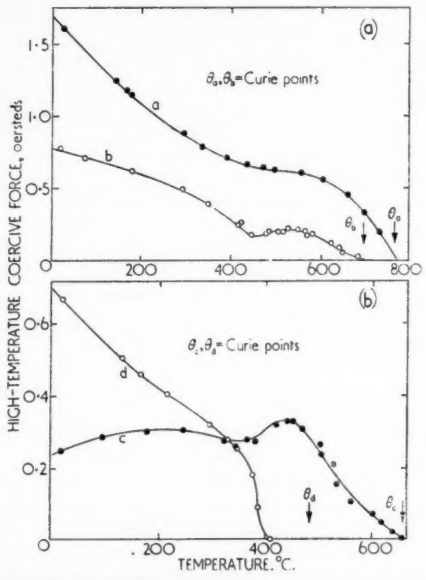


Fig. 10—Coercive-force/temperature curves: (*a*) For iron (type *A*) and alloy No. 12 (17·6% Al); (*b*) for alloys Nos. 15 and 16 (21·5% and 26·9% Al, respectively)

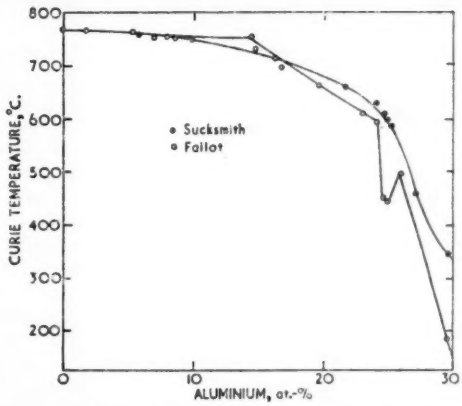


Fig. 11—Curie temperatures *vs.* alloy composition

Curve *c* of Fig. 10*b* shows the variation of coercive force with temperature for alloy No. 15 (21·5% Al). There is an appreciable rise in coercive force over the critical temperature range, although the effect is small in comparison with that in 25% Al alloys. An interesting feature of this curve is the position of the maximum at about 450° C., which is considerably lower than the maxima on the graphs for alloys nearer to the superlattice Fe_3Al. This lower temperature range corresponds with that for the anomalous change in resistivity (*see* Fig. 5).

The change in coercive force with temperature for an alloy with a Curie point below the order–disorder critical temperature is shown as curve *d* in Fig. 10*b*.

For alloys in the immediate neighbourhood of the 25% Al alloy Fe_3Al, the peak was similar to that in Fig. 9 but reduced in size by the proximity of the Curie point. It appeared that alloy No. 13 (25·8% Al) had a much greater peak than alloy No. 14 (24·5% Al). This must result from the presence of FeAl type of order in alloy No. 13, even when it is above the critical temperature, as this is the only real difference between the two alloys.

The coercive force appeared to fall to zero at the Curie point for all alloys containing less than 24·3% of aluminium. Above this level the coercive force fell to zero at a temperature lower than that of the Curie point. This difference is accounted for by the steep portion of the anhysteresis curve (where the irreversible magnetization takes place) moving out to beyond the maximum field strength of 30–40 oersteds. This is to be expected with increasing coercivity, and explains the premature fall in the apparent coercive force.

Measurements were made of saturation magnetization σ per unit mass at different temperatures, using the ring balance. The Curie points obtained were in close agreement with those found by Sucksmith[7] (*see* Fig. 11). Fallot's[8] low values of the Curie point within the superlattice region may arise from the

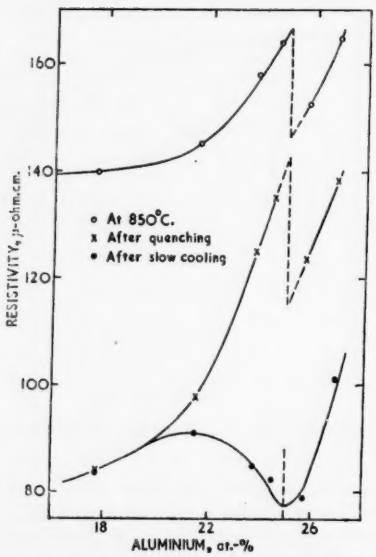


Fig. 12—Resistivity *vs.* alloy composition

fact that he extrapolated the portion of the σ/T curve below the critical temperature.

Typical σ/T curves, which were plotted for two alloys just below the 25% Al composition, showed that the effect of disordering near the critical temperature was to delay the precipitous fall in intensity of magnetization.

DISCUSSION

Since all the anomalous changes in resistivity, coercivity, and saturation intensity of magnetization take place in the temperature range 450–560° C., it is reasonable to assume that they are connected with the precipitous ordering and disordering of the body-centred structure which theory predicts in this region.

Resistivity measurements give the first indication of the way in which this ordering is taking place. At the critical temperature of ordering there is a rise, instead of a fall, in resistivity, which persists in the region of maximum ordering before falling steeply to a low room-temperature value. This behaviour suggests that ordering takes place in small, out-of-phase nuclei; these will not show up as resistance changes but will set up local stresses in the lattice, which, combined with the boundary effect between nuclei, will produce an initial increase in resistance. It is not until one phase of order becomes predominant that the fall in resistance due to ordering becomes effective. This explanation of the initial rise in resistivity is very useful when interpreting the coercivity/temperature results.

Another interesting feature emerges from the resistivity measurements when these are plotted against alloy composition (*see* Fig. 12). Annealed alloys at room temperature have resistivities which lie on a curve showing a dip at the 25% Al composition; it is here that almost 100% order exists. The corresponding values for quenched alloys at room temperature lie on a curve which appears to have a discontinuity at the Fe_3Al composition. This is striking confirmation of the Bradley-Jay results referred to on p. 374 (*loc. cit.*, Fig. 5). At 18·6% Al (10 wt.-%) the curves for quenched and annealed alloys separate, indicating the commencement of order in the annealed alloy. At 25% Al there is a drop in the curve for the quenched alloys, corresponding to the change from the random state to partial order (FeAl type of order) shown by Bradley and Jay. This FeAl type of order, which forms in quenched alloys containing more than 25% of Al, persists at temperatures as high as 850° C., as indicated by the curve for resistivities at this temperature, which is very similar to the curve for quenched alloys.

To sum up, there is a relatively large increase in coercive force in exactly the same temperature region as that in which the anomalous increase in resistivity occurs. This increase is a maximum for alloys near the Fe_3Al composition. The final drop in coercive force is of little significance and may be attributed initially to the maximum applied magnetic field being too small to measure the increasing coercive force, and finally to the sudden fall in magnetic induction at the Curie point.

For an explanation of this rise in coercive force, it is necessary to consider the various theories of magnetization. These may be divided into two main classes: firstly, the so-called 'stress' theories, which take into account the change in energy of a domain boundary, on moving in an applied field, due to variations in intrinsic stress and to change in effective area of the boundary; and secondly, the theories involving purely rotational magnetization in isolated independent domains.

A theory of the second type, recently suggested by Stoner and Wohlfarth,[9] accounts for some of the exceptionally high coercivities that occur in certain alloys. This theory is developed for a hypothetical alloy, in which spontaneously magnetized particles are present in a less magnetic matrix, these particles being below the critical size for which domain boundary formation is possible. Such magnetized particles will act as single domains, the magnetization process being purely rotational and the amount of irreversible magnetization being determined by the degree of magnetic anisotropy of the particle and by the number and orientation of directions of easy magnetization. Factors that give rise to magnetic anisotropy are the shape of the particle, magneto-crystalline effects, and strain, but the first of these produces the largest coercivities. Stoner and Wohlfarth have calculated the effects of shape anisotropy when the particles have the form of ellipsoids.

It was thought at first that this theory could be used to explain the increase in coercivity, assuming small nuclei of disordered alloy in an ordered alloy, but saturation magnetization/temperature curves show that the difference between the magnetization of ordered and disordered alloys is not nearly sufficient to justify an interpretation on these lines.

The earlier stress theories developed by Becker[10] and others seem to be much more promising. At room temperature the difference between the lattice parameters of ordered and disordered alloys is about 5 in 3000. If small nuclei of disordered alloy are

present in the ordered alloy, considerable local stresses will be set up as a result of this change in density. The temperature range in which the large coercivities occur is the range in which the alloy is partially ordered and where zones of ordered and disordered alloy will be present. Assuming that at 500° C. the stress relief due to plastic flow is not appreciable and the changes in lattice parameter are of the same order of magnitude as those at room temperature, this mixture of ordered and disordered alloy will produce a periodic field of stress, which, on the Becker theory, accounts for the increase in coercive force.

A general way of developing this domain-boundary movement theory is to consider the energy associated with a boundary between two domains with the magnetic vectors orientated at 90° or 180° to each other. In this boundary the direction of the electron spins will suffer a gradual transition from one direction to another, and the energy associated with it will be a function of the interchange interaction energy J per unit volume, the lattice parameter a, and an energy factor C. For a specimen, under tension σ, of a material whose saturation magnetostriction coefficient λ is independent of direction and whose magnetocrystalline anisotropy is small, C may be expressed by $C = \lambda\sigma$. Where the magnetocrystalline anisotropy effect is predominant, another expression for C is applicable.

It may be shown that the boundary energy E per unit area is given by :

$$E = c_1 a (JC)^{\frac{1}{2}},$$

where c_1 is a constant depending on precise conditions, such as relative orientation of magnetic vectors in adjacent domains.

Whether or not the strain energy is greater than the crystal energy, the variation in the boundary energy with displacement will be primarily due to variations of internal stress. It can be shown that E is greater for a 180° boundary than for a 90° boundary, and also that the energy involved in a 180° boundary movement is the greater when intrinsic stresses are present. Such boundary movements are therefore the ones which determine the coercive force.

In the absence of a field, the boundary will occupy a position where E is a minimum. With an applied field the boundary will occupy a position where the sum of the field energy and the boundary energy is a minimum. Confining the discussion to a 180° boundary in the yz plane, $dE/dx = 2HI_0$, where H is the applied field and I_0 is the saturation intensity of magnetization. As H increases it will reach a critical value H_0 at which dE/dx is a maximum ; *i.e.* :

$$H_0 = \frac{(dE/dx)_{max}}{2I_0}.$$

Without further increase in field strength, the boundary will advance spontaneously and irreversibly to a new position of equilibrium. If, as mentioned above, the variation of E with displacement is due chiefly to the presence of localized internal stresses, dE/dx can be related to the amplitude of the stress variation.

Kersten[11] considered the effects of various stress distributions, and obtained an expression for a maximum value of H_c (the appropriate average of H_0 throughout the material) :

$$(H_c)_{max} \simeq \frac{3\lambda\sigma_i}{2I_0},$$

where σ_i is an average value for the amplitude of the periodic intrinsic stress distribution. Kersten has since extended this theory to take into account the change in the effective surface area of a boundary, due to the presence of non-magnetic impurities.

It would be useless to make a quantitative comparison of the above theoretical expression and the values of coercive force obtained experimentally, without making measurements of λ and σ_i at different temperatures. Assuming that a small nucleus of disorder is formed in an ordered alloy and that the change in lattice parameter is similar to that at room temperature, an estimate of σ_i could be obtained if Young's modulus were known. It was hoped to be able to have available magnetostriction results at different temperatures, but this has not yet been possible. These results, combined with values of Young's modulus, would make it possible to confirm that the mechanism of increased coercivity is as described above.

The difference in coercive force and hysteresis loss, at room temperatures, between quenched alloys and annealed alloys is not readily explained. In quenched specimens a large tensional hoop stress has been shown to exist, by the formation of gaps when the rings crack. On the Becker theory such an externally applied stress, sufficient to swamp the normal internal stresses, would create large domains with only 180° boundaries. The magnetization vectors would be directed parallel or anti-parallel to the hoop stress, and this would result in a rectangular-shaped hysteresis loop. The fact that quite the reverse occurs on quenching, the hysteresis loop being tilted towards the H axis and the hysteresis losses being reduced, suggests one of two things : either the external stresses produced on quenching (due to shrinkage) do not determine the easy directions of magnetization, or there are radial stresses present. The latter alternative would result in a large measure of rotational magnetization and would explain the gradual approach to saturation in the quenched specimens, but unfortunately it is not in agreement with the observation that a cracked ring springs open. An interesting check on the proportion of 90° and 180° boundaries could be obtained by studying the magnetostrictive behaviour of the alloy in low fields.

Acknowledgment

This research was carried out in the Department of Physics, Sheffield University, under the direction of Professor W. Sucksmith, D.Sc., F.R.S.

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LETTER TO THE EDITOR

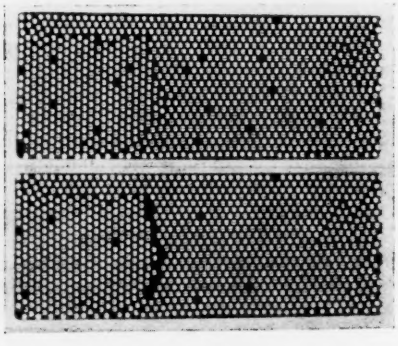
INTERCRYSTALLINE CRACKING OF METALS

The mode of initiation of cracks internally in metals, whether under prolonged application of internal or external stress, under fatigue conditions, or even in a 'static' tensile test, has always presented a difficulty to the writer. The suggestion is now made that cracks are caused by the aggregation of vacant lattice sites.

Recent work on diffusion of metals has indicated the possibility of the creation of vacant sites in metals and alloys because of the greater rate of diffusion of one kind of atom as compared with another. It has further been suggested that the porosity formed in such cases is due to the coalescence of these vacant sites. The view generally held, which seems quite reasonable, is that even in crystals of an annealed metal, there are many vacant lattice sites existing.

It is now suggested that under the joint action of stress and thermal movement of the atoms these vacant sites can migrate. In the higher melting-point metals this may need an elevation of temperature.

If it is postulated (i) that these empty spaces migrate preferentially in the direction of a tensile stress, and (ii) that grain boundaries across which a tensile stress is maintained can more readily accommodate vacant sites, the latter would accumulate in boundaries which lie at right angles to the stress direction.



The end effect is shown in the accompanying figures. The two photographs show: (*a*) 1000 balls arranged on two orientations with 18 vacant sites; and (*b*) the same balls arranged so that ten of the vacant sites are accumulated at the change of orientation.

When a sufficient number of vacant sites has accumulated in any boundary, conditions for the breaking of the cohesive bonds will have occurred, *i.e*,. an intercrystalline crack will have started, which would then open out under the continued stress.

The conditions for intercrystalline cracking would then appear to be

(i) increased temperature
(ii) decreased rate of strain.

The former of these conditions permits mobility of the vacant sites, and the latter creates time for their migration. It will be recognized that these are precisely the conditions which lead to intercrystalline cracking by creep. The term 'migration' is used rather than diffusion because a vacant site, having no prescribed shape, can reappear anywhere in the lattice when it has been displaced by an atom occupying it. Hence the migration would in general be more rapid than diffusion.

A simple calculation shows that this mechanism for the formation of intercrystalline cracks does not make excessive demands on the number of vacant sites available.

Consider a crystal of the order 0·1 mm. linear dimension. There will be approximately 3×10^5 rows of atoms in each axial direction. If each row contained two vacant sites, *i.e.*, one vacant site in 150,000, there would be sufficient to separate completely by two atomic distances an area of boundary surface 0·1 mm. square.

As soon as an area of boundary surface has lost its cohesion *i.e.*, a crack has started, the increased stress along the periphery of the area will aid the propagation of the crack. This hypothesis would then explain the initiation of intercrystalline cracking under those creep conditions which are known to cause it. It would equally explain the initiation of the tertiary stage of creep, whether in tension or compression.

It is known that the creep resistance of metals can be increased by strengthening the crystals by alloying. It is now suggested that the prevention of migration of vacant sites, or the reduction of their number, would lead to reduction in the incidence of intercrystalline cracking.

From work done in this laboratory, it is evident that some solutes inhibit cracking and others accelerate it: *e.g.*, thallium in lead reduces, whilst tellurium greatly increases, the liability to intercrystalline cracking.

A further point is that it suggests why short-time creep tests may not give the same answer as long-time tests.

These thoughts are put down in the hope of stimulating discussion, and giving new lines for experiment in this important field.

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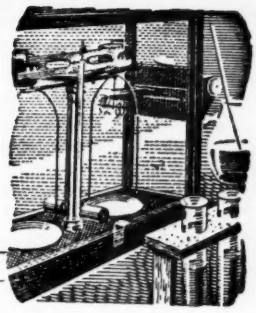

The Effect of Emissivity and Flame Length on Heat Transfer in the Open-Hearth Furnace

By M. W. Thring, M.A., F.Inst.F., F.Inst.P.

SYNOPSIS

Recent developments in port design and the aerodynamics of flames are taken into account in calculating the optimum flame for the open-hearth furnace. This is done by postulating a simplified furnace and flame, and calculating in detail the temperatures along the flame and the roof. Certain simplifying assumptions are necessarily made in the calculations. Four types of flame are considered, each for three different fuel-input rates, and the comparison indicates the optimum flames for three distinct phases of the open-hearth process—charging, melting, and refining.

STATEMENT OF THE PROBLEM

The single-uptake furnace port,[1] the use of oil firing, and other developments have altered the situation in relation to the problems of emissivity and flame length from that disclosed by research in 1946,[2] where the flames were all much too long. Recent work on the aerodynamics of flames[3] and the heat transfer from them[4] has begun to show the principles underlying the control of the course of combustion and the emissivity as the flame passes down a furnace, such as an open-hearth furnace. Both these questions have been investigated in the experimental flame-radiation furnace at Ijmuiden,[5] and the methods of controlling mixing, the predominant factor in deciding combustion length, have been studied with cold-air models.[3]

It is thus important to make a detailed examination of the question of the ideal flame length and emissivity for the O.H. furnace, since there is now a prospect that a good approximation to this ideal can be obtained from the results of other researches. The attempt is being made to evaluate the effect of changing the flame conditions in the O.H. furnace upon the output and fuel economy of the open hearth by empirical experiments, using the factorial method.[6] By this statistical technique important results can be obtained, in spite of the large scatter inherent in industrial trials. Although the empirical method must clearly be the final resort, it is desirable not to have to rely entirely upon it, owing to the difficulty of altering the flame over a wide range of conditions without upsetting production, and owing to the inherent scatter. Experiments recently carried out[7] on an O.H. furnace without steel can greatly reduce the inherent scatter and enable the flame to be altered over a wide range, but this remains a costly method of obtaining the general answer to the question. It is therefore highly desirable to attempt to develop a theoretical method for evaluating the heating rate and furnace-roof temperatures along the length of different types of flame, and the overall fuel economy. This treatment has the further advantage of comparing the prospective performance of quite new designs of furnace with existing designs.

The present report accordingly presents a theoretical treatment based on certain simplifying assumptions, by which the effect of varying the emissivity/distance and the combustion/distance curves can be evaluated. The types of curve assumed to be possible are based largely on the recent Ijmuiden experiments; the method of calculation is a development of that put forward in an earlier paper,[8] allowing for simultaneous combustion and heat transfer according to the equations recently proposed in another.[9]

Since the purpose of the theory is essentially to obtain comparative effects rather than to predict precisely the absolute melting times and fuel consumption which will occur, a number of simplifying assumptions can be made, in so far as these are chosen so as to have about the same relative effects on the different types of flame. The geometry of the system can be greatly simplified provided that the

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Mr. Thring is Head of the Physics Department of the Association.

essential features, such as the fact that the flame flows along the surface of the bath and spreads from a narrow beginning to the full width of the bath at the end, are included.

List of Symbols

T_f Temperature at a given point along the flame, ° C.
T_{f_1} Flame temperature at the beginning of the given zone, ° C.
ΔT_f Change in flame temperature in the zone, ° C.
$\overline{T}_f$ Mean flame temperature in a given zone, ° C.
T_R Temperature of roof and walls assumed only to vary with distance along the furnace, ° C.
T_{f_0} Flame temperature for adiabatic combustion, ° C.
w Width of bath (14 ft. in the numerical example), ft.
f Fraction of width of bath covered by flame (shown as function of distance along flame in Fig. 1).
h Height of roof (7 ft. in the numerical example), ft.
σ Stefan-Boltzman constant, C.H.U./° K.^{4}/sq. ft./hr.
d Flame thickness, ft.
θ_f, θ_s, θ_R Mean absolute temperatures of flame, steel, and wall in the given zone, ° K.
α_1, α_2 Angles subtended at the point on the roof by the mean flame width and the bath respectively.
NR Net heat flow by radiation to the roof, C.H.U./sq. ft./hr.
k Specific flame emissivity, ft.$^{-1}$
ϵ Flame emissivity or absorption for normal radiation.
ϵ' Flame emissivity or absorption for radiation from all directions.
c Heat capacity of oil–steam mixture after evaporation, C.H.U./° C./lb. of oil.
c' Heat capacity of products of combustion of fuel with 150% of theoretical air, C.H.U./° C./lb. of oil.
c'' Heat capacity of 150% of theoretical air for 1 lb. of oil, C.H.U./° C./lb. of oil.
NS_1 Net heat flow to the steel at a point under the flame, C.H.U./sq. ft./hr.
NS_2 Net heat flow to the steel at a point not under the flame, C.H.U./sq. ft./hr.
$\overline{NS}$ Mean net heat flow to the steel combining part under the flame and part not, C.H.U./sq. ft./hr.
$\overline{ns} = \dfrac{\overline{NS}}{1000}$
$\overline{\overline{ns}}$ Mean net heat to steel over whole bath, $\times 10^3$ C.H.U./sq. ft./hr.
Δl Element of length of the flame and furnace, ft.

$$g = \sqrt{2}\sin\alpha_1 = \frac{\sqrt{2}f}{\sqrt{1+f^2}}$$

k, C Constants in equation (5).
m Fuel-input rate, lb./hr.
Δx Fraction of fuel burnt in section Δl.
x' Fraction of fuel burnt at the beginning of Δl.
H_0 Heat of combustion of fuel at absolute zero, C.H.U./lb.
t_{1+2} Time to melt 100 tons of steel, hr.
η Thermal efficiency, total heat going to the steel per hour expressed as percentage of calorific value of fuel burnt per hr.

ASSUMPTIONS TO PROVIDE A SIMPLIFIED MODEL

Types of Flame

It is assumed that heat transfer is by radiation only. This assumption is not entirely accurate and will be considerably in error when the scrap is piled up. Since, however, the critical period in heat transfer is that when the piles have sunk below the surface of the liquid slag, but before the submerged solids are fully melted, the assumption will bring out the desired effects. Generally speaking, a large convection effect would imply the advantage of a shorter flame.

Four types of flame are postulated as simplified models of the flames that actually occur in the open hearth. These are shown diagrammatically in Fig. 1, which indicates for each of the four types the assumed relation between distance along the furnace and

(i) Fraction of complete combustion (x)
(ii) Normal emissivity (ϵ), and
(iii) Flame width as fraction of furnace width (f).

In all four types the flame is assumed to spread as a thin wedge from zero width at the beginning of the heating surface to the full width of the heating surface at the far end, *i.e.*, it is a triangular sheet in every case. In types 1 and 2 the process of combustion, measured by the proportion of the combustible that is burnt, is assumed to proceed uniformly from zero to unity in the first third of the length of the furnace and then to remain constant.* In types 3 and 4 the proportion of the combustible that is burnt is assumed to proceed uniformly along the whole length of the heating surface. Actually the proportion of the combustible burnt will proceed by a hyperbolic curve, but the assumption of uniform combustion serves to show clearly the effect of the long and short flames.

Each type of flame is calculated for different fuel-input rates. If the fuel-input rate were changed with

* Actually combustion proceeds uniformly with distance, and then slows down as the combustion air is used up, but a reasonable approximation to the actual curves for fast- and slow-combustion flames is obtained by taking the two lines as assumed here.

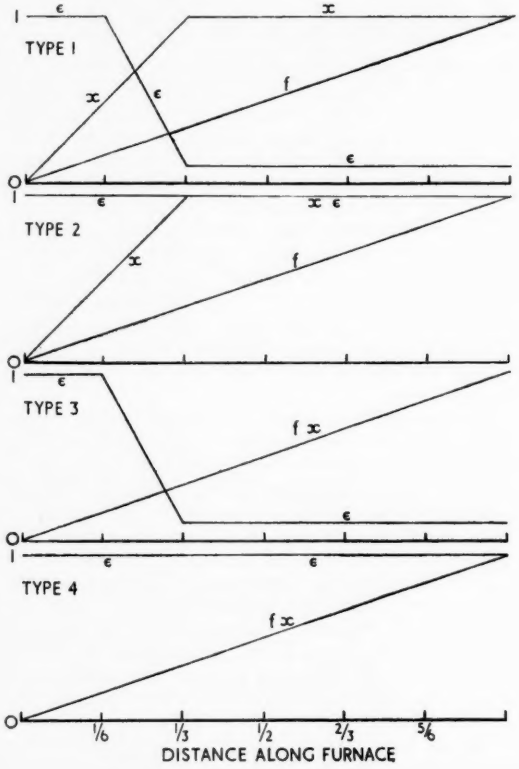


Fig. 1—The four types of flame

a given burner the flame length and emissivity would also be changed; thus the comparisons must be applied between flames at the given input rates and with the given characteristics, and not between flames with a fixed burner.

In types 1 and 3 the normal emissivity of the flame is assumed to be unity in the first sixth of the furnace and to remain constant at 0·10 for the remainder. This type of emissivity curve is chosen as a result of the Ijmuiden experiments, where the emissivity was found to be uniform in the early part of the flame and to fall off steadily as combustion proceeds, finally reaching the non-luminous value at about the point where combustion is complete. The non-luminous value of 0·10 is somewhat lower than would occur in practice, but this is chosen deliberately to accentuate the effect of change from low to high emissivity. In types 2 and 4 the emissivity is assumed to be unity along the whole length of the flames. Type 1 corresponds to the usual effect of rapid combustion where the emissivity falls off as combustion is completed. Type 2 corresponds to the artificial assumption that high emissivity of flame can be maintained in spite of the combustion being completed early on. Type 3 corresponds to the case of delayed combustion in which, nevertheless, the emissivity is lowest early in the flame, and type 4 corresponds to delayed combustion in which the emissivity is maintained high all the time. In all the calculations the heat transfer in each zone of one-twelfth or one-sixth of the furnace is assumed to be that given by the mean emissivity, flame width, and mean flame temperature in that zone. The flame temperature is assumed to vary linearly in each zone so that the mean temperature

$$T_f = T_{f1} + \frac{\Delta T_f}{2} \qquad \text{.....(1)}$$

The value of ΔT_f must be calculated from the heat balance for the zone.

The calculation is carried out for a zone of one-twelfth of the furnace length where the flame temperature is changing with a marked curvature, and a zone of one-sixth of the length where the change is effectively linear.

Assumptions about the Geometrical Conditions on Radiation

In these calculations, as in the previous one,[8] longitudinal radiation is neglected, *i.e.*, each section of flame is supposed to radiate to its own section of walls, roof, and charge only. The physical meaning of this assumption is that the net transverse radiation between two sections is assumed to be zero. This assumption is certainly not accurate, as shown by the Shotton experiments[6] with four calorimeters along the bath, but the effect of balancing transverse radiation is to accentuate differences in temperature and radiation between the different sections, and so to show more clearly the effects of non-uniform heating on roof and charges. In the present paper it will not, however, be assumed that the sections are infinitely wide in comparison with their height, since it is required to take account of the effect of a flame which does not spread across the whole width of the furnace. It will, however, be assumed that the refractory bounding the sides and top of the furnace chamber at any distance along the chamber is at a uniform temperature T_R, whose value is governed by the balance of radiation falling on it and conduction through it. Conduction through it is, however, assumed to be independent of the inside temperature and to be uniform at 2000 C.H.U./sq. ft./hr. As was shown in the previous paper, this conduction constitutes only a small fraction of the gross radiation, and the figure chosen corresponds to rather thin walls. Since conduction depends primarily on the difference between the inside and outside temperature of the brick, and the inside temperature lies in all cases between 1300° and 1700° C., the error in assuming that conduction is always the same will be relatively small and will certainly produce no bias.

A diagram of the cross-section of the furnace with the flame in it is given in Fig. 2. The flame is assumed to have the geometrical shape of a very thin layer with emissivity ε to normal radiation covering a fraction fw of the width w (= 14 ft.) of the bath. The height of the roof is taken to be $h = 7$ ft. Each of the six sections is taken to be 7 ft. long. These dimensions correspond very roughly to a bath area of 588 sq. ft. (the bath is here taken to be rectangular), which would have a capacity in practice of 80–100 tons. An important simplification is also introduced by replacing the fourth powers of temperatures that occur in the radiation equations by approximate linear equations. This is done by taking the equation of the line which passes through the points for 1500° and 1700° C. on the curve for black-body radiation against temperature. The errors are indicated by Fig. 3. The resulting equation is

$$\sigma\theta_f^4 \cong 264\ T_f - 297{,}000 \text{ C.H.U./sq. ft./hr.} \qquad \text{.....(2)}$$

where θ_f is the absolute flame temperature (° K.). The errors due to this assumption are quite small in the important range of temperatures 1350–1800° C. The equation is used outside this range of temperatures on the grounds that it will not alter the relative effects of changing the flame conditions.

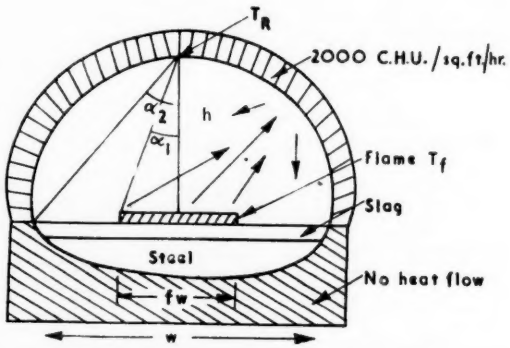


Fig. 2—The assumed-radiation model

Combustion Conditions

The fuel is assumed to be oil with a net calorific value of 9880 C.H.U./lb. atomized with ½ lb. of steam per lb. of oil. This corresponds to a fairly common industrial figure in practice of about 5 lb.

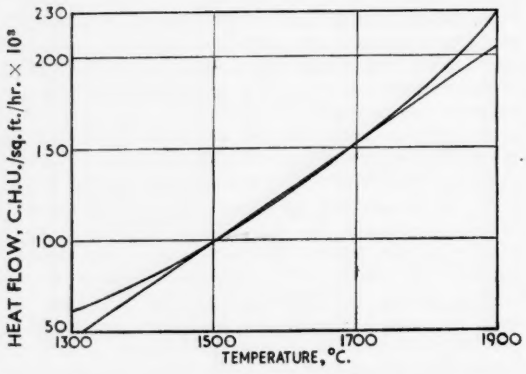


Fig. 3—Linear approximation to the black-body radiation curve

of steam per gal. of oil. It is assumed to be burnt with 50% excess air, the air being supplied to the furnace from the checkers with 1000° C. preheat. This means that for each lb. of oil, 21·0 lb. or 260 cu. ft. (at N.T.P.) of air are supplied. This air is supposed to have a heat capacity of 0·022 C.H.U./° C./cu. ft., so that the air corresponding to 1 lb. of fuel has a heat capacity c'' of 5·71 C.H.U./° C./lb. of fuel. The products of combustion are assumed to consist of the gases shown in Table I together with their heat capacity. The total heat capacity c' of the fully burnt gases is 6·63 C.H.U./° C./lb. of fuel. It is assumed that the oil/steam mixture is heated to 500° C. by radiant heat transfer from the walls of the furnace between leaving the end of the burner and starting combustion over the beginning of the bath. This heat, which corresponds to 905 C.H.U./lb. of fuel, is supposed to be recycled, *i.e.*, it is extracted from the outgoing combustion gases in passing the corresponding place at the other end of the furnace between the end of the bath and the port. This part of the furnace is therefore assumed to act as a kind of regenerator. Whilst this assumption is qualitatively correct as compared with the real furnace it may not be quantitatively correct; it will not, however, alter the relative effects appreciably. The heat capacity of the evaporated fuel stream is assumed to be $c = 1{\cdot}17$ C.H.U./° C./lb. of fuel.

All these heat capacities are based on the mean heat capacities of the respective gases between 0° and 1500° C., but are assumed to be constant over the whole range of temperatures. This assumption is not at all accurate above 1700° C., but if the temperatures calculated above that are regarded as parameters in the equations rather than as real temperatures, the assumption of no increase in heat capacity to a large extent cancels that of a linear heat-transfer coefficient on the actual heat transfer, and the relative effects will certainly be correct. This means that the real temperatures one would measure in a flame are lower than the calculated ones by an amount which increases rapidly from zero above 1700° C.

Combustion is assumed to proceed in the same manner as postulated previously,[9] *i.e.*, the air stream flows alongside the fuel stream, retaining its initial temperature but gradually losing material to the fuel stream. In fact, this assumption is an over-simplification. The air will be heated by convection as it passes along the furnace, and it will also be mixed with recycled combustion gases. It is difficult to estimate how much effect these factors will have, but they will probably reduce the advantage of rapid combustion by a certain amount. The change in temperature of the fuel stream is a balance of heat release by combustion and heat loss to the surroundings. In general its temperature therefore rises to a peak and then falls, the shape of the curve depending entirely on the rapidity of combustion and heat transfer. The heat capacity of the flame gases rises as combustion proceeds, changing from that of fuel-steam alone *via* an increasing mixture of some unburnt fuel with steam plus some burnt products plus excess air, and finishing with all burnt products plus 50% of excess air. The mixture can be calculated from the postulated combustion curve at any point using the assumption that 50% more air is entrained at each zone than is required for the combustion in that zone.

Assumptions about the Steel and Slag

In the present calculations only a rough account has been taken of the effect of the thermal resistance of the slag and metal, emphasized in an earlier paper,[10] by assuming that the surface temperature of the slag is 1500° C. all along. This temperature is high enough to accentuate the fact that the furnace roof will overheat if the flame radiation is too high in any section, although the assumption will give results which are not quite so severe on the roof as would result from the assumption that the steel is at a constant temperature of, say, 1400° C., whilst the slag layer has a thermal resistance so that its surface temperature depends on the heat transfer through it at any point.

Assuming the surface temperature of the slag to be uniform throughout the bath also implies that if the flame cools excessively, there can be a portion of the bath where the steel is actually providing the heat necessary to maintain the roof at its temperature and prevent the flame cooling further. Such a case would not occur in practice, and it can therefore be laid down that whenever the heat transfer from flame to metal becomes negative it would be necessary in practice to increase the fuel-input rate. This remark does not apply to the one-sixth of the furnace length where the flame starts at 500° C. and receives heat in all cases from the metal. It would have been

Table I

COMBUSTION GASES FROM 1 LB. OF FUEL

	Vol. cu. ft./lb. of Oil	Mean Specific Heat 0°–1500° C., C.H.U./° C./cu. ft.	Heat Capacity, C.H.U./° C./lb. of Oil
CO_2	26·0	0·0350	0·91
H_2O	21·1	0·0274	0·58
N_2	137·3	0·0217	2·97
Excess air	87·0	0·0219	1·90
H_2O (atom)	9·9	0·0274	0·27
		Total	6·63

simpler to assume that combustion is adiabatic in this zone; this would make little difference to the final answer (all the curves for different fuel-input rates for one type of flame would then coincide in these zones), except to give smoother curves in the first three zones; it seems slightly less plausible than to assume the same heat-transfer mechanism in zone 1 as elsewhere.

DEVELOPMENT OF THE EQUATIONS FOR HEAT-TRANSFER AND FLAME-HEAT BALANCES

Radiation Equations for a Given Cross-Section

From the assumptions made on p. 383 and shown in Fig. 2, it follows that the net heat transfer by radiation to a point on the inside of the roof on the axis in a given zone, and to a point under the flame, can be evaluated.

The expressions are greatly simplified if the variation of the apparent blackness of the flame, according to the angle at which it is viewed, can be neglected without obscuring the effects which are being sought. To see what effect replacing this has on the integrals, the radiation to the steel rather than that to the roof can be considered. This will show the greatest effect and it is simpler, since here the double integral can be replaced by a single integral using annular rings (subtending an angle γ at the point on the steel) as the elements of area, so that an integrated absorption is obtained, which can be evaluated for each value of ε from 0·1; the result is shown in Fig. 4. It appears from this that ε' is always higher than ε, except when $\varepsilon = 0$ and 1, when they are equal, as would be expected. Even when $\varepsilon = 0{\cdot}5$, ε' is only 0·67, so that the comparison between flames with $\varepsilon = 0{\cdot}1$ and $\varepsilon = 1{\cdot}0$ will not be greatly affected by replacing ε' by ε. A convenient compromise is therefore to use ε' in the evaluation of NS, where the integration is always over the hemisphere, so that ε', which has been calculated as a function of ε, is the correct absorption to use, but to neglect the variation of flame absorptivity with the obliquity of the path in the evaluation of NR. This is justified for two reasons: firstly, the angle α in the integrals for NR never exceeds $\pi/4$ (since the flame width at the outgoing end of the furnace is just twice the height of the roof), so that approximation will be good; and

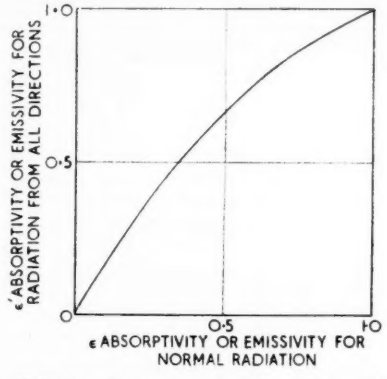


Fig. 4—Relation between normal and hemispherical emissivity

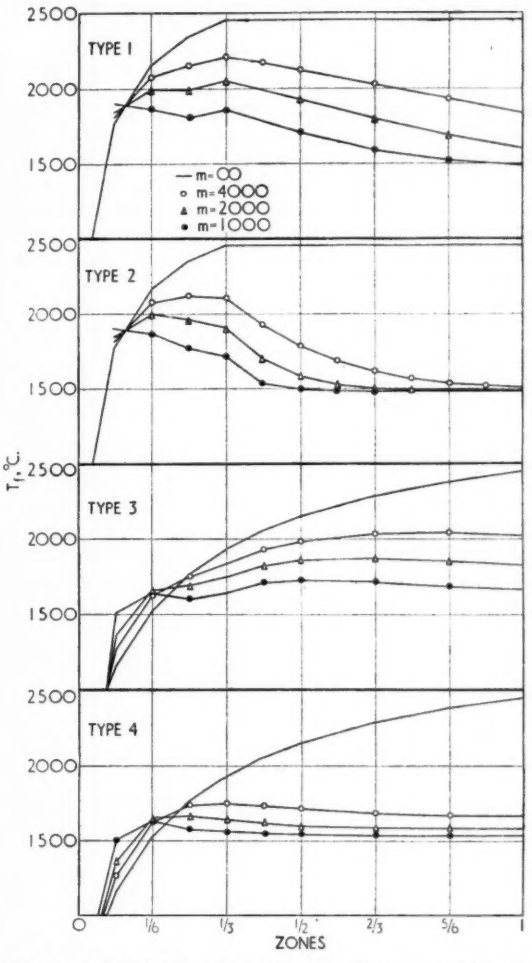


Fig. 5—Calculated flame-temperatures along the furnace

secondly, the assumption already made that NR is equal at all points around the roof and side wall involves an approximation of the same order as this one.

Using this assumption, the expression for the net heat to the roof becomes

$$NR = \sigma\varepsilon\theta_f^4 \sin\alpha_1 + \sigma\theta_s^4 (\sin\alpha_2 - \epsilon \sin\alpha_1) - \sigma\theta_R^4 \sin\alpha_2 \ldots (3)$$

By applying the assumption that $NR = 2000$ C.H.U./sq. ft./hr., using the fact that $\sin\alpha_2 = 1/\sqrt{2}$, an expression is obtained between $\sigma\theta_R^4$ and $\sigma\varepsilon\theta_f^4$ and $\sigma\theta_s^4$. By using the linear approximation (2) for the quartic term, this gives

$$T_R = \epsilon g T_f + (1 - \epsilon\alpha) T_s - 11 \ldots\ldots\ldots\ldots\ldots (4)$$

The mean heat flow to the steel per unit area in a given section $\overline{NS}$ can be similarly calculated as the weighted average of the flows under the flame and at the sides. The resulting equation may be written

$$\overline{ns} \equiv \frac{\overline{NS}}{1000} = k(T_f - T_s) - C \ldots\ldots\ldots\ldots\ldots (5)$$

where $1000k \equiv 264\ (\epsilon'_f + \epsilon g - \epsilon\epsilon' fg)$
$1000C \equiv 2830(1 - \epsilon' f)$

Heat Balance for the Flame along a Short Length of Furnace

The second equation relating T_f and $\overline{NS}$, from which they can be calculated in conjunction with equation (4), is provided by constructing a heat balance for the flame in passing along a length Δl of the furnace. Δl is assumed to be sufficiently short for the heat transfer in this section to be calculated by giving T_f, ε, ε', f, and g their arithmetic mean values for the section. This gives

$$NR(2h + w)\Delta l + NS.w.\Delta l = m\left\{\Delta x\left[H_0 + 1273c'' - \theta_f(c' - c)\right] - \Delta\theta_f \left[c + (c' - c)(x_1 + \Delta x)\right]\right\} \ldots (6)$$

Calculation of Change of Flame Temperature in a Given Section

By inserting 2000 C.H.U./sq. ft./hr. for NR and the value of $\overline{NS}$ given by equation (5) in equation (6), an equation is obtained for ΔT_f, the change in flame temperature in the length Δl of the furnace; $\Delta\theta_f$ is identical with ΔT_f. It is necessary to use the approximation that the heat-transfer temperature T_f used in equation (5) is the arithmetic mean of the initial and final temperatures of the zone, so that T_f is replaced by

$$\overline{T}_f = T_{f_1} + \tfrac{1}{2}\Delta T_f \text{ (equation 1).}$$

This gives

$$\Delta T_f = \frac{\frac{m}{1000}\Delta x\left[H_0 + 1273\,c'' - \theta_f(c' - c)\right] - k.w.\Delta l(T_{f_1} - T_s) - 2(2h + w)\Delta l + C.w.\Delta l}{\frac{1}{2}k.w.\Delta l + \frac{m}{1000}\left[c + (c' - c)(x_1 + \Delta x)\right]} \ldots\ldots (7)$$

This is the equation on which all the numerical calculations are based. The numerical values used are

$c' = 6{\cdot}63$ C.H.U./° C./lb. (*see* Table I)
$c'' = 5{\cdot}71$,, ,,
$c = 1{\cdot}17$,, ,,
$H_0 = 9880$ C.H.U./lb.
$w = 14$ ft.
$h = 7$ ft.
$\Delta l = 7$ ft., or 3 ft. 6 in., according to whether zones one-sixth or one-twelfth of the furnace length are being used.

Then equation (7) becomes

$$\Delta T_f = \frac{\frac{m}{1000}\Delta x(15{,}660 - 5{\cdot}46T_{f_1}) - 14\Delta l.k(T_{f_1} - T_s) - 56\Delta l + 14C.\Delta l}{7\Delta l.k. + \frac{m}{1000}\left[1{\cdot}17 + 5{\cdot}46(x_1 + \Delta x)\right]} \ldots\ldots (8)$$

In the case where the fuel input m is so great that combustion is adiabatic, only the terms with m remain, so that

$$\Delta T_{f_0} = \frac{\Delta x(15{,}660 - 5{\cdot}46T_{f_1})}{1{\cdot}17 + 5{\cdot}46(x_1 - \Delta x)};$$

in particular, putting $x_1 = 0$, $\Delta x = 1$, $T_{f_1} = 500°$ C., the adiabatic temperature for complete combustion is found to be 2450° C., which agrees with that calculated from the equation

$$\theta_{f_0} = \frac{9880 + 1273 \times 5{\cdot}71 + 1{\cdot}17 \times 773}{6{\cdot}63} = 2723° \text{ K.}$$

In all cases where adiabatic combustion is assumed to proceed in stages, the final temperature for complete combustion must agree with this.

DISCUSSION OF RESULTS

Flame Temperature Distance Relationships

Adiabatic Combustion Temperatures—The results o the stepwise calculation of flame temperature for each of the four types of flame are shown in Figs. 5*a–d*. On each of these figures the curve marked $m = \infty$ corresponds to the flame temperature for adiabatic combustion, *i.e.*, the temperature that would be developed along the flame if either

(*a*) There were a normal fuel input but the flame were insulated from the roof and steel, or

(*b*) The fuel input were increased to a very high rate so that the heat transfer from it did not affect its temperature at all.

These curves for adiabatic combustion must in all cases finish at the adiabatic temperature of complete combustion T_{f_0}, which in the present case is approximately 2450° C.

In types 1 and 2 the curve $m = \infty$ is a stepwise approximation to a part of a rectangular hyperbola,[9] reaching the value T_{f_0} after one-third of the length of the furnace, since this is the distance to complete combustion here. In types 3 and 4 it approximates to a part of another rectangular hyperbola reaching the temperature T_{f_0} at the end of the furnace.

Flame Temperatures for the Finite Fuel-Input Rates—In the first one or two zones the flame temperatures for the fuel-input rates 4000, 2000, and 1000 lb./hr. lie above those for adiabatic combustion, since the flame is actually below the steel temperature in these zones and therefore receives heat from the steel. The temperature soon falls below the adiabatic combustion temperature as the flames start to give up heat to the steel. The lower the fuel-input rate, the greater is the temperature drop caused by this cooling effect, since the heat capacity of the flame gases is lower. In types 1 and 2 the flame gases cool steadily once combustion is complete, type 2 giving a much more rapid fall than type 1 owing to the higher emissivity. On the other hand, in types 3 and 4, where combustion is proceeding uniformly throughout the whole length of the furnace, the flame gases tend to reach a fairly constant temperature, at which the heat given up to the roof and to the steel balances the heat liberated by combustion in each zone. This steady temperature for type 4 is much nearer to 1500° C. than for type 3 because the heat transfer corresponding to a given temperature difference is nearly ten times as great in type 4 as in type 3.

Table II

MEAN NET HEAT FLOW TO STEEL, 10^3 C.H.U./SQ. FT./HR., AND ROOF TEMPERATURE, °C., FOR EACH SECTION

Zone	Type 1 (Rapid Combustion, Falling Emissivity)						Type 2 (Rapid Combustion, Maintained Emissivity)						Type 3 (Slow Combustion, Falling Emissivity)						Type 4 (Slow Combustion, Maintained Emissivity)					
	$m = 4000$		$m = 2000$		$m = 1000$		$m = 4000$		$m = 2000$		$m = 1000$		$m = 4000$		$m = 2000$		$m = 1000$		$m = 4000$		$m = 2000$		$m = 1000$	
	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R	$\overline{ns}$	T_R
1.1	−11·7	1469	−11·3	1470	−10·6	1471	−11·6	1468	−11·3	1469	−10·6	1471	−18·8	1452	−17·6	1454	−15·6	1459	−18·8	1452	−17·6	1455	−15·6	1459
1.2	30·0	1567	28·5	1563	25·7	1557	30·0	1567	28·5	1563	25·7	1556	−6·1	1480	−1·52	1491	3·02	1502	−6·1	1478	−1·52	1491	3·02	1502
2.1	55·6	1625	44·9	1599	29·8	1563	66·2	1668	52·9	1627	34·2	1580	16·1	1532	14·8	1529	9·39	1517	19·3	1543	17·1	1538	10·44	1521
2.2	38·7	1573	29·4	1554	17·9	1531	86·0	1723	60·4	1635	33·1	1583	15·7	1527	11·1	1517	5·17	1504	34·1	1585	21·3	1551	8·66	1518
3.1	17·4	1523	12·5	1514	6·81	1504	91·3	1745	52·6	1649	22·0	1551	8·6	1508	5·75	1503	2·57	1497	42·9	1611	22·5	1556	9·08	1519
3.2	20·1	1527	13·4	1516	5·96	1503	71·8	1700	27·0	1571	1·35	1498	13·4	1516	9·50	1509	5·17	1502	44·9	1622	21·7	1556	8·74	1518
4	22·5	1531	13·1	1516	3·93	1501	43·4	1624	6·66	1513	−3·74	1481	19·5	1526	13·5	1516	7·25	1506	45·1	1631	20·7	1558	9·07	1520
5	23·1	1531	10·7	1509	0·62	1493	17·1	1548	−2·00	1485	−4·02	1478	26·2	1534	17·0	1519	8·47	1506	44·0	1638	20·8	1561	8·70	1520
6	21·5	1525	6·9	1503	−1·92	1489	4·6	1507	−3·52	1478	−3·91	1476	30·8	1539	18·8	1521	8·69	1505	42·7	1645	21·4	1565	8·72	1521
$\overline{ns}$	23·7		14·9		6·73		38·7		17·7		6·87		15·1		10·1		4·88		31·7		15·8		6·44	
t, †, hr.	5·02		8·00		17·7		3·15		6·73		17·3		7·88		11·8		24·4		3·76		7·54		18·5	
η, %	35·2		44·3		40·1		57·6		52·6		40·9		22·5		30·0		29·1		47·1		47·0		38·3	
Fuel to melt 100 tons, lb.	20,100		16,000		17,700		12,600		13,500		17,300		31,500		23,600		24,400		15,000		15,100		18,500	

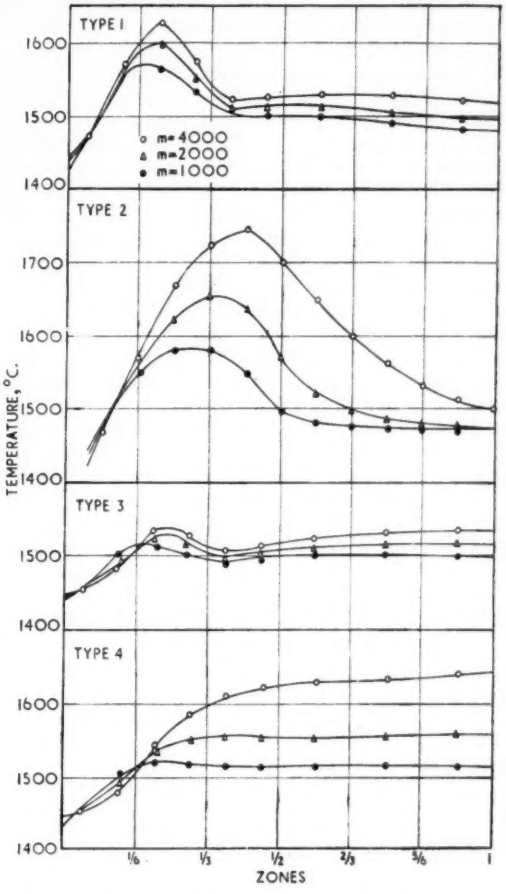


Fig. 6—Roof temperatures along the furnace

The small kinks in the early part of the flame arise from the kinks in the shape chosen for the emissivity distance curve for types 1 and 3.

Net Heat Transfer to the Steel and Roof Temperature along the Furnace

The calculated values for the net heat transfer to the steel, in thousands of C.H.U./sq. ft./hr., and for the roof temperature for each section of the furnace, are given in Table II for each of the four flames, each with three fuel-input rates. The variation of net heat transfer to the steel along the furnace is not of great significance; it is rather the overall heat transfer which affects the value of any given flame to the furnace operator. On the other hand, the variation of roof temperature along the furnace is of great importance, since a local peak temperature will cause fusion of the roof. The calculated roof temperatures are therefore shown plotted as a function of distance along the furnace in Figs. 6*a–d*, from which it will be seen that type 1 flame shows a very sharp peak temperature on the roof, about one-sixth of the way along the furnace, which falls off mainly because of the rapid falling-off in emissivity. Type 2, where there is no fall-off in emissivity, shows an even higher

peak in the flame temperature, occurring just about at the point where combustion is complete, the roof temperature thereafter falling off simply because of the drop in flame temperature. Type 3 shows a slight tendency for a peak roof temperature where the emissivity is high at the end of zone 1, as in type 1, and then a final rise in roof temperature when the flame spreads across the whole width of the bath. Type 4 simply shows a steady rise in roof temperature because the spreading of the flame across the bath more than offsets the small fall in flame temperature.

With rapid combustion (types 1 and 2) the net heat transfer to the steel ($\overline{NS}$) becomes negative at the end of the flame when the fuel-input rate is low, and especially when the emissivity is high. This means that the flame is receiving heat from the steel, although in fact it receives less heat from the steel than it gives to the roof; hence the flame temperature drops in all cases along the flame. The heat transfer from the flame to the roof just balances that from the steel to the flame when the NS is -4 (-4000 C.H.U./sq. ft./hr.), since the heat transferred to the roof has been taken to be 2 in these units and the area of the roof in each section is just twice the area of the bath.

Overall Heat Transfer to the Steel and Thermal Efficiency

In the last four rows of Table II are given respectively:

(i) The mean values for the net heat transfer to the steel ($\overline{NS}$) in 10^3 C.H.U./sq. ft./hr. for the whole bath for each of the 12 calculated curves;
(ii) The time (t_{1+2}) in hr. to melt 100 tons of steel with this net heat transfer;
(iii) The thermal efficiency (η), *i.e.*, the total heat going to the steel per hr. expressed as a percentage of the calorific value of the fuel put in per hr.; and
(iv) The fuel used to melt in lb.

The time for melting (t_{1+2}) has been calculated on the assumption that one lb. of steel needs 310 C.H.U. to melt it, so that 100 tons require 7×10^7 C.H.U. Hence

$$t_{1+2} = \frac{7 \times 10^4}{\overline{NS} \times 588} \text{ hr.}$$

$$\eta = \frac{\overline{NS} \times 588 \times 1000}{m \times 9880} \times 100\,\%$$

Fuel used to melt $= m \times t_{1+2}$

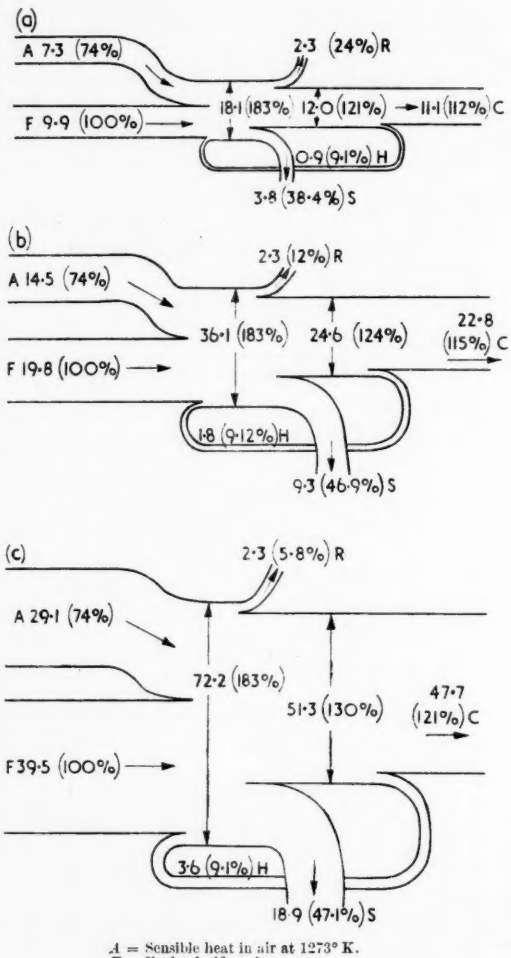
The calculated melting times cover the range which occurs in practice, although the thermal efficiencies are rather higher than are obtained in practice, principally because the slag surface-temperature rises higher than the value of 1500° C. assumed here towards the end of the melting period, and the completion of melting is delayed with a consequent loss of thermal efficiency. It will be seen that the thermal efficiency (η) regarded as a function of fuel-input rate for each type of flame, in the case of flames 1 and 3 with falling emissivity, is highest for the middle value, *i.e.*, 2000 lb./hr. For the two flames with the emissivity maintained constant (types 2 and 4) η is highest for the highest fuel-input rate, *i.e.*, 4000 lb./hr. This is a consequence of an effect studied in an earlier paper,[10] where it was shown that in general the efficiency of a furnace rises at first as the fuel-input rate is increased from zero, because the wall heat losses absorb a smaller fraction of the energy, and then for higher heat-inputs falls because the heat-transfer bottleneck between the flame and the charge causes the chimney losses to rise. Hence one expects a flame with a higher heat-transfer coefficient to give the optimum efficiency at a higher fuel-input rate.

Figure 7 shows Sankey diagrams for the overall heat-balance of the furnace for type 4 flame at the three fuel-input rates, the figures on the various energy streams representing the energy flow in 10^6 C.H.U./hr., and the figures in brackets the energy flow as a percentage of the calorific value of fuel input.

CONCLUSIONS

Importance of the Type of Flame

The diagrams for roof temperature (Fig. 6) and



A = Sensible heat in air at 1273° K.
F = Fuel calorific value
R = Heat lost through roof
C = Sensible heat in exit gases to checkers
H = Recycled heat to fuel stream
S = Heat to steel

Fig. 7—Sankey diagrams for type 4 flame; fuel-input rate: (*a*) 1000 lb./hr.; (*b*) 2000 lb./hr.; (*c*) 4000 lb./hr. All sensible heats expressed above absolute zero

the calculated melting times given in Table II show clearly that it is of the utmost importance from all the three criteria from which the performance of an O.H. furnace is judged to have the flame with the right emissivity and the right combustion length. These three criteria are:

(i) To give the greatest possible output of molten steel, *i.e.*, the shortest possible melting time
(ii) To use the lowest possible amount of fuel per ton of steel melted, and
(iii) To avoid melting the roof at any point along its length.

While many of the assumptions made to reduce the problem to tractable proportions clearly do not correspond exactly to the conditions in an O.H. furnace, the fact that the roof temperatures and melting times are of the right order of magnitude shows that a general picture has been built up which may be used with some confidence for assessing the effects of changing these flame conditions. If the thermal conductivity of the slag and its thickness were accurately known, it would be preferable to replace the assumption made here of a uniform slag temperature by an assumption that the steel temperature was uniform while the slag temperature was determined by equating the heat flow to the slag with that through it. Calculations on such an assumption would show a reduced heat transfer at the places where this is greatest, because the slag temperature would be highest at these places, but it would tend to increase the roof temperatures still more. This assumption would therefore probably have the effect of reducing the permissible fuel-input rate at which local overheating of the roof was avoided, but should not affect the comparison between the four types of flame very much.

Optimum Flame in the Open-Hearth Furnace

The calculations support the view held by most practical steelmakers that the optimum flame in the open-hearth furnace is different at different stages in the melt, and it will therefore be discussed under a separate heading for each stage. The calculations indicate different optimum flames during the three periods when

(i) There is so much cold metal in the furnace that the roof temperature nowhere exceeds the safe maximum (1660° C. for a silica roof). This is the period when the surface is far from flat, and is not at 1500° C., and convection is important, so that the model used here is least closely applicable to this case
(ii) The maximum fuel rate is set by the roof reaching the safe temperature at one point, but it is still desirable to pump heat into the bath as rapidly as possible to melt the charge right through, including that necessary to heat the bath to melt the submerged solid metal. This period is often the greatest obstacle in the whole process
(iii) The charge no longer needs heat, and the problem is to keep the whole furnace at the working temperature with the minimum fuel-input rate.

These three periods correspond roughly to the charging, melting, and refining periods, and so they will hereafter be described by these names.

The general principle can be laid down that the upper limit of fuel-input rate for any given type of flame is set by the roof overheating at one point, and the lower limit by the flame temperature falling below the steel temperature at the tail of the flame. The latter does not occur over the whole range of fuel-input rates examined when combustion proceeds uniformly throughout the length of the furnace, whilst the former is much more liable to occur with a flame with a high emissivity than with one with a low emissivity, as concluded in an earlier paper.[8] Flames of type 3, *i.e.*, with a low emissivity and delayed combustion, can be operated over an extremely wide range of fuel-input rates without reaching either of the extreme conditions. At the other end of the scale, flames of type 2 with a high emissivity and rapid combustion have hardly any fuel-input rates at which both overheating and negative heat transfer to the steel at the tail are avoided.

Optimum Flame During Charging

At the stage when the maximum fuel-input is set by air and fuel supply conditions and not by the roof temperature, flames of type 2, with the highest possible fuel-input rate at which the requirement of combustion complete in one-third of the furnace can be satisfied, are the best, since they give the highest overall heat transfer to the steel and the highest thermal efficiency. The introduction of a convection term would also lead to the desirability of the shortest possible flame, but would not also require a high emissivity.

Unfortunately, there is at present no known way of producing flames where the emissivity is maintained high throughout the length of the furnace while combustion is completed in the first third. In practice therefore the choice usually lies between flames of type 1 and type 4, *i.e.*, between rapid combustion with a falling emissivity or slow combustion with a maintained emissivity. In this case the flames of type 4 are clearly the better for radiant heat transfer, *i.e.*, a long flame with maintained high emissivity gives a more rapid heat-input to the steel for a given fuel-input than rapid combustion with falling emissivity. There is, however, clear scope for improvement if a method can be found from the Ijmuiden work for maintaining the emissivity of a flame at a fairly high level even though combustion is effectively complete, *e.g.*, by producing some soot particles which do not disappear for some time after the remainder of the fuel is fully burnt out. These conclusions are subject to the proviso that this stage corresponds least to the model chosen, but a reduction of the steel surface temperature accentuates the need for a high emissivity in the flame.[3]

Optimum Flame for Melting Down

The conditions governing the time between finish charging and fully melted may be taken to be those where the roof is at the safe maximum temperature at its hottest point, the fuel being adjusted to avoid exceeding this, and the problem is to obtain the required heat transfer as quickly as possible during this period.* The roof-temperature figures of Table II

* As already pointed out, an actual burner with fixed orifice will not give identical flame-lengths at all fuel-input rates. This does not, however, affect the argument, which simply leads to the conclusion that the best burner is that which will give a flame of type 4 at 4000 lb./hr.

show that the flame with rapid combustion but maintained emissivity at a fuel rate of 4000 lb./hr. gives temperatures exceeding 1660° C. from early in the second zone to early in the fourth zone,* *i.e.*, for a third of the furnace, the peak being slightly before the centre of the furnace. Hence with a silica roof this type of flame cannot be used above about 2000 lb./hr. fuel-input rate. On the other hand, none of the other flames show temperatures exceeding 1660° C. at any point, even at 4000 lb./hr., although the flame of type 4 with delayed combustion and maintained emissivity gives a roof temperature just reaching 1660° C. at the outgoing end. Ruling out therefore the 4000 lb./hr. of type 2, the next best flame for rapidity of melting is the 4000 lb./hr. of type 4 with slow combustion and maintained emissivity, which gives a melting time of 3·76 hr., although the best flame from the point of view of thermal efficiency is type 2 at 2000 lb./hr. Thus if rapidity of melting is the primary consideration the delayed-combustion flame with maintained emissivity (type 4) is the best in this period, followed by type 3 (rapid combustion with low emissivity), each at 4000 lb./hr. If minimum fuel consumption is the primary consideration, rapid combustion with 2000 lb./hr. gives the best results. The further conclusion can be drawn that the optimum flame length would be slightly shorter than that of type 4, which gives a steadily rising roof-temperature. By interpolation one can estimate that the optimum flame length for an expanding flame of the type considered here is about three-quarters of the length of the furnace, and combustion should proceed uniformly in this distance. This provides a definite goal for aerodynamic research on mixing, and hence combustion, in this type of flame. It also indicates a method for testing when the combustion in the flame proceeds in the optimum distance, *i.e.*, to use two roof pyrometers sited a quarter and three-quarters of the way along the furnace and to adjust the flame length until they read the same, while the quantity of fuel is adjusted so that they both read the safe maximum for the roof.

With oil flames it is possible to shorten the flame length, as shown in the 1949 Ijmuiden trials, by using air instead of steam as atomizing agent and increasing the jet momentum by changing burner design or increasing the atomizing agent proportion. This suggests that the next step in automatic control of O.H. furnaces should be a control system involving two roof pyrometers, in which the one reading higher controls the fuel quantity, as at present, but with the addition that the difference between them controls the jet momentum.

The roof-temperature curves shown in Fig. 6 also indicate that the all-basic roof can make more use of a high-emissivity flame than can a silica roof. This follows because flames of types 2 and 4 give a roof temperature rising more sharply as the fuel quantity is increased than do those of falling emissivity of types 1 and 3. Thus, with the all-basic furnace, high emissivity and a high fuel-input rate can give a big increase in melting rate, but to conserve fuel the flame must be shortened in comparison with a silica roof: probably combustion should be complete in just over half the length of the furnace.

Optimum Flame During Refining

The refining period may be taken as when the purpose of the flame is not to supply an appreciable amount of heat to the bath, but simply to maintain the bath temperature all along. The best flame is therefore that which gives the flame temperature above 1500° C. in all except the first zone, with the lowest fuel-input rate. From this point of view the curves of Fig. 5 show that there is nothing to choose between flames of type 3 and type 4, since in neither does the flame temperature drop below 1500° C., even at 1000 lb./hr. fuel-input rate. To check this point further one can calculate the condition that the fuel-input rate shall be such that the heat liberated by burning one-sixth of the fuel in the zone at the tail of the flame (zone 6) shall be just equal to the heat given to the roof in this section. This calculation gives a fuel-input rate of 315 lb./hr., so provided that the fuel-input rate exceeds this value, neither of the flames with delayed combustion (types 3 and 4) will drop below 1500° C., since this is the flame temperature at which the heat transfer to the steel is zero. Thus there is in principle no advantage in high emissivity during the refining period, but delayed combustion is even more important than it is during the first two periods, since it is the only way by which the flame temperature can be kept from falling below the steel temperature at the tail of the flame when the fuel-input rate is very low. This calculation can be carried further to show that if the net heat flow is zero to the last section with delayed combustion, the mean flame temperature in this section must be 1538° C. for the low-emissivity flame and 1501° C. for the high-emissivity flame. This marked difference arises because the high-emissivity flame spreads across the whole furnace at this point, and the steel only ' sees ' the flame and not the roof; hence little temperature difference is required to make up the small amount of heat which the steel can transmit to the roof.

A tentative extension of this argument suggests that low emissivity is probably better than high for refining, because if the flame length is difficult to maintain equal to the full length of the furnace the low-emissivity flame will tend to degenerate to type 1, whereas the high-emissivity flame will tend to degenerate towards type 2, which is much more liable to give excessive cooling of the flame at the tail than type 1.

Other Types of Flame

This method of calculation can of course be applied to many other types of flame, but even without carrying out such application in detail it is possible to draw qualitative comparisons for some other types of flame by regarding them as combinations, and interpolating between the types considered here. Three cases are discussed:

(i) A flame of coke-oven gas might be taken as a flame having an emissivity of 0·2 all the way along. If such a flame were burnt with rapid combustion it would correspond to something intermediate between types 1 and 2 at the tail of the flame, but without the high peak of roof tempera-

* A zone is one-sixth of the furnace length.

tures occurring in the first two sections of type 1. Thus the roof-temperature and flame-temperature curves would be generally similar in shape to those of type 2, but the former would be scaled down closer to 1500° C. along its length. Such a flame would be not so good as the optimum high-emissivity one (type 4) for melting down, but would be excellent for refining if the combustion length could be extended to the whole length of the furnace.

(ii) The flame which would be produced by the use of three oil burners spaced across the end of the furnace, giving approximately a parallel sheet-flame covering the whole width of the bath all along instead of the model taken here of one spreading uniformly from a narrow width at the ingoing end. This parallel flame would give higher roof temperatures in the first two zones than occur in the present calculations, and it would thus render slow combustion more essential with a silica roof: in fact the optimum length for melting down would be the full length of the furnace, *i.e.*, exactly type 4.

(iii) The cross-fired furnace proposed by Seil, in which a large number of small flames proceed across the furnace. This would automatically give roof and flame temperatures uniform along the length of the furnace, although the latter would rise to a very high peak in going across the furnace. The smoothing-out action of the flame being well down from the roof would probably avoid overheating of the roof, so that the advantages of a uniform flame would be obtained, but it would still be desirable to make the emissivity of the flame as high as possible during the melting-down period.

Effect of Preheat and Excess Air

Whilst no detailed calculations have been made in the present paper on the effect of varying preheat and excess air, the same method could be used for selected flames, and the fact that with the present assumptions of 50% excess air and 1000° C. as the preheat, the sensible heat of the air (above 0° C.) contributes 5700 C.H.U. to every pound of oil burnt, while the calorific value of the latter is 9880, shows the importance of obtaining the maximum possible preheat. Likewise the fact that the 50% excess air contributes 1·90 to the total heat capacity of waste gases from 1 lb. of fuel of 6·63 C.H.U./° C./lb. shows the tremendous effect of the excess air on the flame temperatures.

APPENDIX

Estimation of the Maximum Error Caused by the Assumption of Balanced Transverse Radiation

A detailed calculation has been carried out for the case where the assumption that oblique radiation between a section and its neighbours balances out is likely to be least accurate. This occurs when there is a sharp peak in the roof temperature, so that the radiation from both sides is less than that of the given section. This is the case of zone 3.1 with flame 2. For this case a closer approximation can be made

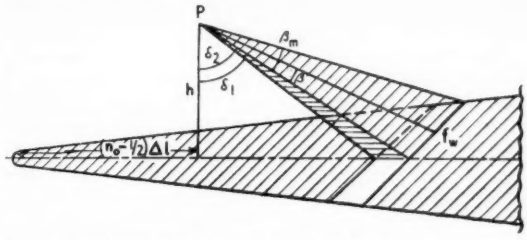


Fig. 8—Oblique radiation to a point *P* on the roof from a strip of flame

using the calculated flame temperatures and evaluating the contribution of each section to oblique radiation. If the bath is divided into 12 strips, these can be treated as narrow, so that the edges of the flame or bath for each strip can be regarded as having a constant value β_m of the angle β in Fig. 8. Then the radiation from a strip of black flame is given by:

$$\Delta R = 2\int_0^{\beta_m} \sigma\theta_f^4 \cdot \frac{1}{\pi}\cos^2\beta[\sin\delta]_{\delta_1}^{\delta_2} d\beta$$

where θ_f is the mean absolute temperature in this section of flame,
δ_1, δ_2 are the values of δ corresponding to the two edges of the strip, and
β_m is the value of β corresponding to the ends of the strip

$$= \sigma\theta_f^4[\sin\delta_2 - \sin\delta_1][\beta + \tfrac{1}{2}\sin 2\beta]_0^{\beta_m}$$

Similarly the radiation from the steel on each end of this strip is given by

$$\Delta R_s = \frac{\sigma\theta_s^4}{\pi}[\sin\delta_2 - \sin\delta_1][\beta + \tfrac{1}{2}\sin 2\beta]_{\beta_m}^{\beta_w}$$

where β_w is the value of β corresponding to the edge of the bath at this strip.

Then if the 12 sections are numbered $n = 1$–12, and n_0 denotes the one whose roof temperature is to be calculated

$$\tan\delta_1 = \frac{\Delta l\{n - 1 - (n_0 - \frac{1}{2})\}}{h} = \tfrac{1}{2}\{n_0 - \tfrac{1}{2} - n\}$$

(since $\Delta l = 3{\cdot}5$ ft., $h = 7$ ft.)

$$\tan\delta_2 = \tfrac{1}{2}\{n_0 + \tfrac{1}{2} - n\} \quad \text{(since } w = h = 7 \text{ ft.)}$$

$$\tan\beta_m = \frac{f.w}{h.\sec\delta_m} = f\cos\delta_m$$

In this way the total radiation which would fall on the roof from a tapering film with θ_f varying along it can be calculated as a second approximation. T_f along the black flame of type 2 with $m = 4000$ has been calculated and compared with that predicted from the simplifying assumption that oblique radiation cancels, *i.e.*, that the radiation in section 3.1 prevailed in all other sections and at the ends. The radiation from the flame falling on the roof is thus found to be 71,400 C.H.U./sq. ft./hr. for the actual flame-temperature distribution with the actual taper flame, 80,400 for a flame of the same shape but with temperature equal to that in 3.1 at all other points, and 80,600 for a flame with temperature and width constant all the way along. The corresponding radiations received from the steel are 34,400, 34,000, and 34,600. Thus, in the worst case the error due to neglecting differences in transverse radiation from the

bath and flame gives the radiation on the roof too high by 9200 C.H.U./sq. ft./hr. in a total of 115,000.

The remainder of the 16,400 units of radiation falling on the roof are those from other points on the roof. These will also be in error in the same direction, since the oblique radiation will be less than that corresponding to the roof temperature of the given section. If, therefore, an upper limit is set to this error by assuming that it is proportional to the error in the flame and bath contribution, it follows that the calculated roof-radiation is too high by $9200 \times 164/115 = 13{,}100$, giving an error in the roof temperature of $13{,}100/264 = 50°$ C. (by equation 1). A third approximation would reduce this estimate of error, since equalizing the roof and flame temperatures by the amount required by the second approximation will make the effects of oblique illumination less. In all other cases where the roof and flame temperatures do not have such a sharp curvature the effect of oblique radiation will be less.

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Determination of Iron in Ores, Slags, and Refractories

By the Methods of Analysis Committee

SYNOPSIS

The stannous chloride reduction method for the determination of iron has been fully investigated and its scope and limitations have been disclosed. A hydrogen sulphide reduction procedure is recommended as being of more general application, and confirmation has been provided by extended trials on synthetic solutions and oxide-type materials. Various decomposition techniques have also been examined and general principles for a suitable choice are indicated. Modifications of the hydrogen sulphide method have been made for application to materials of low iron content and an absorptiometric procedure has been devised for use below 1% of iron.

Introduction

Work on the determination of iron in a variety of materials such as ores, slags, and refractories has been carried out over the past five years by the Blast Furnace Raw Materials and Slags, Steelmaking Slags and Refractories Analysis Sub-Committee. The fundamental reproducibility of each analytical principle selected required examination and the following programme was therefore adopted:

(*a*) Selection of methods; determination of optimum operating conditions; effect of interfering elements, and fundamental reproducibility

(*b*) Application of the final method to a wide variety of oxide-type materials.

This scheme of investigation was applied to the well-known stannous chloride reduction method, which included a dichromate titration with diphenylamine sodium sulphonate as internal indicator. The method was found to be simple and reproducible for relatively pure iron solutions, but subject to interference from certain elements likely either to be present in the sample or to be introduced during analysis. Finally, hydrogen sulphide as a reducing agent for ferric iron provided the basis of a comprehensive procedure for the determination of iron in a wide variety of oxide-type materials.

The stannous chloride method has been retained for general application in the absence of certain interfering elements; its scope and limitations have been fully investigated. The hydrogen sulphide method, although less simple, is recommended strongly as

Paper MG/D/23/52 of the Methods of Analysis Committee of the Metallurgy (General) Division of the British Iron and Steel Research Association, received 21st March, 1952.

Table I

COMPOSITION OF SYNTHETIC IRON-ORE SAMPLE MGS/1

Constituent	Theoretical, %	Actual, %
Fe_2O_3	60	59·36
FeO	—	1·43
SiO_2	10	8·90
Al_2O_3	10	10·08
TiO_2	—	0·01
Mn_3O_4	5	4·74
CaO	10	10·0
MgO	5	5·25
P_2O_5	—	0·037
SO_3	—	0·030
Na_2O	—	0·07
K_2O	—	0·06
Loss	—	Nil

the standard method for the determination of major contents of iron.

These methods are described in Part I and the recommended procedures are given in Appendices I and II.

The determination of iron contents of less than 3% in ores, slags, and refractories has been studied both volumetrically and absorptiometrically. It was thought that, after suitable modifications, the volumetric method developed for major contents of iron might be applicable with reasonable accuracy to low iron contents. On the other hand, it was appreciated that the higher precision required for these low iron contents might necessitate a different approach to the problem; consequently an absorptiometric method, using thioglycollic acid, was also examined. These methods are outlined in Part II, and the recommended procedure for the absorptiometric method will be found in Appendix III.

The constitution of the Sub-Committee at 30th September, 1951, was as follows:

G. E. Speight (*Chairman*)	The United Steel Companies, Ltd.
B. Bagshawe	Brown-Firth Research Laboratories
E. W. Harpham	B.S.A. Group Research Centre
I. Herbert	Richard Thomas and Baldwins, Ltd.
W. H. Hesson	Appleby-Frodingham Steel Co.
A. P. Lunt	Park Gate Iron and Steel Co., Ltd.
D. Manterfield	Steel, Peech and Tozer
N. D. Ridsdale	Bureau of Analysed Samples, Ltd.
C. W. Short	J. Lysaght, Ltd.
J. L. West	Hadfields, Ltd.
T. H. Williams	Stewarts and Lloyds, Ltd.
E. C. V. Wiskar	Dorman, Long and Co., Ltd.
J. O. Lay (*Secretary*)	British Iron and Steel Research Association.

The Sub-Committee is appreciative of the active interest and support of the following past members:

H. R. Pepper	Stewarts and Lloyds, Ltd.
R. Pritchard	Shelton Iron Steel and Coal Co., Ltd.
J. H. Wright	Dorman, Long and Co., Ltd.

Part I — DETERMINATION OF MAJOR CONTENTS OF IRON

STANNOUS CHLORIDE METHOD

Preliminary Trials

The well-known but insufficiently appreciated stannous chloride method was first examined. Typical results for iron in a Cleveland ironstone, which were already on record,* are as follows:

Laboratory	Iron, %
1	33·25
2	32·9
3	33·4
4	33·6
5	33·1
6	33·35
7	33·2
8	33·5

From working details submitted by the co-operators, a 'unified' procedure was formulated and submitted for trial on two samples, *MGS*/1, a synthetic iron ore carefully prepared in the laboratory from a sintered mixture of pure oxides, and *MGS*/2, a commercially pure iron. Their analyses are given in Tables I and II.

The spread of results of these trials, expressed in terms of *N*/10 potassium dichromate, was *MGS*/1, 37·25–38·45 ml.; and *MGS*/2, 89·1–89·6 ml.

For each sample the individual results obtained within a particular laboratory showed closer agreement than did the average results of the different laboratories. The greater spread of results on the synthetic iron ore seemed due to the more complicated decomposition required for this sample. Later work has shown that the major cause of this divergence was platinum, introduced from the crucibles used for the fusion of the insoluble residues.

In further trials on *MGS*/2 each operator used the same standard titrating and indicator solutions, and made the necessary burette corrections for temperature. Typical results showed a range of average results from six operators of 89·0–89·4 ml. of *N*/10 potassium dichromate, although as previously the separate results from each laboratory were in closer agreement.

Investigation of Optimum Conditions

Certain features of the draft method, including the amount of excess stannous chloride solution after

* Co-operative examination by the Raw Materials Analysis Sub-Committee of the British Iron and Steel Federation, 1946.

Table II

COMPOSITION OF HIGH-PURITY IRON MGS/2

Element	Chemical, %	Spectrographic, %
C	0·10	—
Mn	0·02	—
Si	0·028	—
S	0·005	—
P	0·037	—
Ni	—	0·01
Cr	—	0·01
Mo	—	Nil
V	—	0·01
Ti	—	Nil
Sn	—	0·015
Cu	—	0·03
W	—	Nil
Co	—	Nil
Al	—	0·005
O_2	0·125*	—
H_2	0·00003*	—
N_2	0·002*	—
Fe	99·62†	—

* By vacuum fusion † By difference

Table III

EFFECT OF TEMPERATURE ON STANNOUS CHLORIDE TREATMENT

Laboratory	*N*/10 Dichromate,* ml.			
	100° C.	70° C.	40° C.	R.T.
1	44·75	44·7	44·7	44·8
2	...	44·75	...	...
3	44·5	44·5	44·5	44·4
4	44·7	44·7	44·75	44·75
5	44·65	...	...	...
6	44·5	44·5	44·55	44·55
7	44·5	44·5	44·4	44·4
8	44·7	44·65	44·7	44·65
10	44·55	44·55	44·65	44·85
11	44·6	44·65	44·55	44·55
12	44·7	44·75	44·6	44·65

* These titres on 0·25-g. pure iron samples are relative only within each laboratory

reduction of the ferric iron, the quantity of mercuric chloride added, and the standing time after addition of mercuric chloride before titrating, were examined in more detail. Tests were also carried out on the relative merits of oxidized and non-oxidized indicators.

The amount of excess stannous chloride after reduction of ferric iron was not unduly critical. Complete reduction of the iron must be ensured, necessitating an excess of reducing agent, but no effect on the iron result was obtained by using up to 20 drops excess of stannous chloride solution (5%). As the excess is best kept to a minimum, an excess of 3 drops after the ferric iron colour has been completely discharged is recommended.

The amount of mercuric chloride was not critical. Using an excess of 5 drops of stannous chloride solution (5%), no difference in iron result could be detected with a mercuric chloride addition ranging between 6 and 24 ml. of 4% solution. Therefore 12 ml. of mercuric chloride solution (4%) was specified.

The effect of decreased temperature on the stannous chloride reduction, which hitherto had taken the form of a dropwise addition of the reagent to the gently boiling solution, was examined. Tests (*see* Table III) confirmed that the reduction could be effected at temperatures below boiling quite readily, but that when approaching room temperature the rate of reaction became very sluggish, introducing the possibility of over-treatment with stannous chloride. The reduction is therefore carried out in a solution at just below boiling point. This lower reduction temperature was advantageous when vanadium was present.

Using the recommended additions of stannous and mercuric chloride, the effect of variation in standing time between addition of mercuric chloride and titration was significant. There was a tendency to high titres when the standing interval was too short to effect complete destruction of the excess stannous chloride; low results were obtained when the interval was more than 5 min.:

Standing time, min.	1	2	5	10	20
N/10 dichromate, ml.	89·05	89·0	89·0	88·8	88·8

Table IV indicates a positive error with increasing amount of non-oxidized indicator. Thus, using 10 drops the error is about 0·15 ml. of *N*/10 dichromate, although slightly lower errors were reported by some co-operators. For practical purposes the error caused by 5 drops is negligible with large amounts of iron and does not warrant the preoxidized indicator. It cannot be stressed too strongly, however, that for work of the highest accuracy and particularly for relatively small contents of iron, the preoxidized indicator must be used.

Tests were now carried out on B.C.S. sample *A*2, using the final modified method given in Appendix I. The results obtained from nine co-operators show a total spread of 88·95–89·2 ml. of *N*/10 potassium dichromate (Table V). It was considered that this represented the limit of reproducibility possible from the method at this level of iron content.

Effect of Other Constituents

Tests were carried out to determine the effect on the stannous chloride method of elements which might be present either in the original sample or in the final test solution for titration. Known amounts of a pure salt, or of the metal itself, were added to a series of pure iron tests before decomposition of the metallic sample in hydrochloric acid. The iron titres obtained were then compared with those from similar amounts of pure iron without the added elements. The following elements had no significant effect on the iron titre when present to the extent indicated:

Element	Added as:	Maximum Amount Added Element, mg.	% of Element on 0·5-g. Sample
Fluorine	Sodium fluoride*	100	20
Silicon	Sodium silicate	75	15
Phosphorus	Sodium phosphate	50	10
Nickel	Metal	25	5
Cobalt	Metal	25	5

* Added immediately before reduction

Chromium in large amounts interfered only by giving an intense colour in the solution, which impeded visual observation of the end-point of the stannous chloride reduction. Interference may arise from As,

Table IV

BLANK VALUES ON DIPHENYLAMINE INDICATOR SOLUTIONS

N/10 Ferrous Ammonium Sulphate, ml.	Drops of Indicator Used		*N*/10 Dichromate, ml.	Error, ml.
	Non-Oxidized Indicator	Preoxidized Indicator*		
2·0	10	—	2·15	+0·15
2·0	20	—	2·3	+0·3
2·0	30	—	2·45	+0·45
4·0	10	—	4·15	+0·15
4·0	20	—	4·35	+0·35
4·0	30	—	4·5	+0·5
2·0	—	10	2·0	Nil
2·0	—	30	2·05	+0·05
4·0	—	10	4·05	+0·05
4·0	—	30	4·1	+0·1

* For details of the preoxidized indicator solution *see* E. Gregory and W. W. Stevenson, "Chemical Analysis of Metals and Alloys," pp. 248–249. London and Glasgow, 1942: Blackie.

Ti, or W if they occur in reduced form in the final solution, but oxidation by potassium chlorate rules out this possibility. In the presence of Pt, V, Cu, or Mo the iron titres were seriously affected and their separation is essential if correct iron results are to be obtained.*

Platinum—The presence of only 2 mg. of Pt increases the titre by about 1 ml. of *N*/10 potassium dichromate and the error is progressive with increased Pt, until at 10 mg. the normal end-point is completely obscured. The following are typical results:

Pt Added, mg. (0·5-g. sample)	*N*/10 Dichromate, ml.
Nil	89·2
1	89·6
3	90·4
5	91·6[1]
10	—[2]

[1] End-point very indistinct. Probably over-titrated.
[2] End-point indeterminate.

The presence of Pt in an iron test is usually indicated by the yellow colour of chloro-platinous acid in the reduced and cooled solution after addition of stannous chloride. Whilst the possibility of Pt occurring as a normal constituent of iron and steel works raw materials and slags is remote, accidental introduction, *e.g.*, from a fusion decomposition in a Pt crucible, may seriously affect the accuracy of the determination. The precipitation of Pt as sulphide from the acid solution before the stannous chloride reduction of iron gave a satisfactory separation which should be used where the presence of Pt is suspected.

Vanadium—A progressively increased titre is obtained with increasing vanadium content, as shown by the following typical results:

Vanadium Added (on 0·5-g. sample) %	mg.	*N*/10 Dichromate, ml.
Nil	Nil	89·1
1	5	89·5
2	10	91·1
3	15	91·6
4	20	92·0
5	25	92·4

* This interference led ultimately to the investigation of the more satisfactory hydrogen sulphide reduction method.

Table V

IRON RESULTS OBTAINED WITH FINAL STANNOUS CHLORIDE METHOD

(0·5-g. sample B.C.S. 'A2')

Laboratory	*N*/10 Dichromate, ml. (Individual Values)
1	89·2, 89·15, 89·15
2	89·0
3	89·15, 89·2, 89·15
4	89·0
5	89·95
6	89·2
7	89·0, 89·0
8	89·15
9	89·1
Average	89·1
Range	+0·1 / −0·15

The effect arises from the reduction of vanadium below the tetravalent state. The trivalent vanadium produced is subsequently reoxidized to the tetravalent state by potassium dichromate. The effect is not stoichiometric; indeed a mixture of tri- and tetravalent vanadium is obtained, depending presumably on conditions prevailing. Whilst reduction at a lower temperature reduced this positive error, the results were very variable:

0·25 g. of Pure Iron, 12·5 mg. of Vanadium

	N/10 Dichromate, ml.				
	100° C.	70° C.	40° C.	R.T.	H_2S Method
Average titre	46·2	45·5	45·45	45·3	44·65
Range of 12 co-operators	47·25–44·9	46·75–44·70	46·75–44·85	46·7–44·45	44·8–44·4

As it is not possible to define clearly the conditions which control the reduction of vanadium below the tetravalent state during the reduction of ferric iron by stannous chloride, to obtain iron results of the highest accuracy either the vanadium must be separated or an alternative procedure must be sought. The effect of vanadium was best overcome by using hydrogen sulphide as the reducing agent in preference to stannous chloride.

Copper—It is not possible to give typical results for the effect of Cu on the iron titration, as there are two opposing tendencies, one towards high and the other towards low results; under certain conditions it may be possible to have no apparent effect from Cu. The high results are presumably attributable to the presence of cuprous ions in the solution before titration, whilst the low results are said to arise from the catalytic effect of Cu on the atmospheric oxidation of ferrous salts.

In the tests carried out no error was detected with less than 2 mg. of Cu present, but the greatest positive error was 1·6 ml. with 25 mg. of Cu, and the greatest negative error 0·55 ml. with 5 mg. of Cu.

The tendency towards high or low results is probably mainly associated with the time of standing after additions of mercuric chloride to destroy excess stannous chloride. Precise definition of this time factor in relation to the amount of Cu present would become so difficult that it is preferable to remove the Cu as the sulphide before reduction of ferric iron; for special work, the hydrogen sulphide method described later is recommended.

Molybdenum—The presence of Mo leads to high results for iron by the stannous chloride method. Within the normal limits of Mo in iron ores or steel-making slags, etc., the effect is small; typical results are as follows:

Molybdenum Added (0·5-g. sample) %	mg.	*N*/10 Dichromate, ml.
Nil	Nil	89·2
0·2	1	89·3
0·8	4	89·5
1·2	6	89·6
2·0	10	90·4

The presence of appreciable amounts of Mo in the iron solution after reduction with stannous chloride gives rise to a greenish solution which on dilution turns yellow. For general work the removal of small amounts of Mo, *e.g.*, less than 2·5 mg., would not be

necessary and the stannous chloride method without modification is applicable.

The decreased stannous chloride reduction temperature also assists in reducing the effect of Mo, but with more than 2·5 mg. separation is necessary, and a double ammonium hydroxide or sodium hydroxide precipitation of the ferric iron can be employed. Precipitation of Mo as sulphide from acid solution by the procedure outlined in the following section is also satisfactory, and as this treatment compensates for the effects of other interfering elements, *viz.*, Pt, Cu, V, it is recommended for samples containing Mo.

Chromium—As Cr does not interfere directly, the stannous chloride method can be safely applied to solutions containing normal amounts of this element. If, however, the Cr content is such as to yield a highly coloured green solution, the completion of the stannous chloride reduction stage becomes difficult to judge, and there is some danger of either incomplete reduction of iron or an abnormal excess of stannous chloride. Hydrogen sulphide, therefore, is to be preferred as a reducing agent for high Cr contents. Visual observation of the titration end-point is not difficult in the presence of Cr.

Arsenic, Titanium, and Tungsten—These elements interfere in the iron determination if present in their reduced forms in the solution before titration; in fact, under such conditions seriously high iron titres may be obtained. Oxidizing the initial solution of the sample by treatment with potassium chlorate guards against the possibility of interference from these elements. This aspect of the potassium chlorate treatment in the stannous chloride method has generally received little appreciation.

Acid Radicals—Sulphuric, perchloric, and boric acids have no effect on either stannous chloride reduction or on the final titration when carried out as recommended in Appendix I. Nitric acid interferes with the stannous chloride reduction, although minor nitrate impurities can be tolerated, and if this acid must be used in the decomposition stage it should be eliminated before the ferric iron reduction. The presence of phosphoric acid tends to give low iron titres, due presumably to the formation of weakly ionized ferric phosphate which resists reduction by stannous chloride. The effect is not significant with the amounts of phosphoric acid likely to arise from a phosphorus-rich sample, but with major amounts of the acid, which might be used to decompose a particular sample, the effect assumes greater significance. Typical results are as follows:

Phosphoric Acid (sp. gr. 1·75), ml. (0·5-g. sample)	*N*/10 Dichromate, ml.	
	$SnCl_2$ Method	H_2S Method
Nil	89·3	89·2
0·3	...	89·1
1	...	89·2
2	89·15	...
5	...	80·5*
10	88·85	66·2*
20	88·55	49·6*

* Averages of figures showing a very wide spread—reproducible results could not be obtained.

For accurate iron determinations, therefore, phosphoric acid is best omitted from the decomposition procedure.

Fluorine or hydrofluoric acid have no direct effect on the stannous chloride method. However, hydrofluoric acid may introduce errors if the decomposition is carried out in glassware. The following figures give an idea of the possible magnitude of this effect:

Solvent acid: 30 *ml. HCl*, 10 *ml. HF. Digestion time:* 1 *hr.*

Glass Type	Wt. Loss of Glass Vessel, g.	*N*/10 Dichromate, ml.	Fe in Glass, %
A	4·338	2·0	0·26
B	4·268	0·6	0·08
C	4·000	0·75	0·105

Final Trials on Miscellaneous Samples

The stannous chloride method, as finally modified (*see* Appendix I), has been applied to a wide selection of blast-furnace raw materials and slags, steelmaking

Table VI

FINAL TRIALS OF STANNOUS CHLORIDE METHOD ON IRON-ORE SAMPLES

Iron, %

Laboratory	MGS/80	MGS/81	MGS/82	MGS/83	MGS/84	MGS/85	MGS/86	MGS/87	MGS/88	BCS/244	BCS/245	BCS/175
	Kiruna	Cleveland	Djerissa	Sproxton	Lincolnshire	Hematite	Mysur-Orne	Sierra Leone	Wabana	Magnetite	Hematite	Standard Iron Ore
1	65·6	30·6	57·3	42·2	24·7	40·0	43·8	57·05	52·35	56·05	34·2	58·1
2	65·4	30·5	57·3	41·9	24·8	39·85	43·5	56·8	52·6	55·4	33·65	58·05
3	65·5	30·65	57·3	42·1	25·05	40·1	43·8	57·05	52·55	56·05	34·2	58·2
4	65·15	30·75	57·25	41·85	24·9	40·05	43·6	56·75	52·35	...	...	...
5	65·4	30·9	57·25	42·2	25·1	40·4	43·9	57·1	52·7	55·65	34·2	58·2
6	65·4	30·65	57·35	42·2	24·7	40·0	43·75	56·75	52·6	55·65	33·7	58·0
7	65·4	30·65	57·3	42·1	25·05	40·1	43·8	57·05	52·55	55·8	33·8	58·1
8	65·2	30·5	57·0	42·1	24·7	40·1	43·6	56·6	52·6	55·8	33·75	58·1
9	...	...	57·0	42·0	25·0	40·2	43·55	56·7	52·6	...	...	58·05
10	65·55	30·85	57·3	41·95	25·15	40·0	43·85	56·5	52·6	55·9	33·9	57·95
11	65·2	30·6	57·0	42·0	24·7	40·0	43·6	56·5	52·5	56·0	34·1	58·15
12	65·2	30·85	56·9	42·0	25·3	40·35	43·8	56·7	52·5	55·8	33·8	58·1
Average	65·4	30·7	57·2	42·05	24·95	40·1	43·7	56·8	52·55	55·8	33·95	58·1
Deviation +	0·2	0·2	0·15	0·15	0·35	0·3	0·2	0·3	0·15	0·25	0·25	0·1
Deviation −	0·25	0·2	0·3	0·2	0·25	0·25	0·2	0·3	0·2	0·4	0·3	0·15

slags, and refractories, with the results given in Tables VI and VII. As these trials have also involved detailed consideration of decomposition procedures, and were carried out in conjunction with similar trials of the hydrogen sulphide method, further discussion is deferred.

HYDROGEN SULPHIDE METHOD

The work on the stannous chloride method indicated that the most effective way of dealing with the interference of Pt, Cu, Mo, and V was by treatment with hydrogen sulphide, which removes the first three elements as sulphides and produces tetravalent vanadium which has no effect on the iron titration. For samples containing significant amounts of these interfering elements, it was decided therefore to incorporate a hydrogen sulphide treatment in the stannous chloride method. It was realized that hydrogen sulphide would also reduce ferric iron but, in view of possible difficulties in eliminating hydrogen sulphide whilst still retaining iron in a reduced condition it was believed that the reduced solution after elimination of hydrogen sulphide would still require treatment with stannous chloride. This was shown to be unnecessary and a method using hydrogen sulphide as the sole reducing agent was developed.

Stability of Ferrous Iron after Reduction by Hydrogen Sulphide

Preliminary trials on pure iron solutions indicated that hydrogen sulphide as a substitute for stannous chloride in the reduction of iron was effective. Experiments have shown that ferrous iron reduced by hydrogen sulphide is quite stable in dilute sulphuric or perchloric acid solutions, but far less stable in hydrochloric acid solution. Typical results for dilute acid solution (Table VIII) show that excess hydrogen sulphide is readily eliminated by 8–12 min. boiling,

Table VIII

STABILITY OF FERROUS SULPHATE UNDER THE CONDITIONS OF THE HYDROGEN SULPHIDE METHOD

Laboratory	Boiling Time, min.	Cooling and Standing Time	*N*/10 Dichromate (0·5-g. Sample), ml.	
			CO_2 Atmosphere	Covered Flask
1	20	15 min.	89·15	89·2
	20	4½ hr.	—	89·2
	20	18 hr.	—	89·15, 89·25
2	20	10 min.	89·2, 89·1	89·2, 89·1
	70	10 min.	—	89·1
		18 hr.	—	89·0
3	20	10 min.	89·25, 89·2	89·2, 89·25

and that further boiling up to 60 min. in a flask covered only by a small watch glass has no effect on the iron titres. The time of cooling and standing, again without special precautions to exclude air, can be extended to 18 hr. without measurable effect. The final recommendation to boil until a lead acetate paper gives a negative test—approximately 10 min. —followed by a further 10 min. boiling has been fully confirmed by later work.

Effect of Other Constituents

Those elements having no effect in the stannous chloride method are similarly without effect in the hydrogen sulphide method.

Platinum and Copper—No difficulties were encountered in synthetic tests on pure iron with the

Table VII

FINAL TRIALS OF STANNOUS CHLORIDE METHOD ON MISCELLANEOUS SAMPLES
Iron, %

Laboratory	MGS/147	MGS/100	MGS/101	MGS/102	MGS/103	MGS/104	MGS/105	MGS/106	MGS/107	MGS/108	MGS/129	MGS/139
	Basic Slag	Basic Slag (F-Bearing)	Basic Slag	Acid Slag	Aluminous Clay	Manganese Ore	Chromite	Chrome-Magnesite Brick	Tap Cinder	Sinter	Bauxite	Turkish Chromite
1	9·1	8·05	12·2	6·3	7·15	15·1	18·2	8·1	49·5	42·8	15·85	11·2
2	9·15	7·85	12·1	6·1	7·05	14·9	18·15	8·1	49·3	42·65	15·6	11·3
3	9·1	7·85	12·05	6·2	7·05	15·0	18·25	8·0	49·6	42·6	15·85	11·2
4	...	...	...	...	...	...	...	...	...	...	15·75	11·2
5	9·25	8·0	12·15	6·2	7·1	15·0	18·2	8·2	49·8	42·7	15·8	...
6	9·0	7·95	12·05	6·3	7·1	14·85	18·2	8·0	49·9	42·95	15·7	11·1
7	9·25	8·05	12·2	5·95	7·1	15·05	18·15	8·2	49·6	42·7	15·7	11·2
8	9·3*	7·85*	12·0*	6·2	7·0	15·2	18·1	8·3	49·4	42·7	15·95	11·5
9	...	8·0	12·2	6·2	7·1	15·0	18·1	8·1	49·7	42·7	...	...
10	9·35†	7·7	11·85	6·1	7·15	14·95	18·0	8·1	49·95	42·95	16·0	11·2
11	9·15	8·05	12·15	6·15	6·9	15·1	18·25	8·2	49·6	42·7	...	...
12	9·15	8·15	11·9	6·15	7·2	15·1	...	8·2	49·8	42·65	15·8	11·3
13	9·0	...	...	...	...	...	...	...	...	...	...	...
Average	9·15	7·95	12·1	6·15	7·1	15·0	18·15	8·15	49·65	42·75	15·8	11·25
Deviation +	0·2	0·2	0·1	0·15	0·1	0·2	0·1	0·15	0·3	0·2	0·2	0·25
Deviation −	0·15	0·25	0·25	0·2	0·2	0·15	0·15	0·15	0·35	0·15	0·2	0·15

* Reduction at 70° C.: 9·0, 7·6, 11·7% Fe respectively. (These three samples have up to 1% V present—see p. 395)
† Reduction at 70° C.: 8·85% Fe

addition of up to 25 mg. of Cu or 5 mg. of Pt. Separation of the sulphides during the reduction of iron was complete and the final solutions gave accurate iron titres.

Vanadium—Tests of the hydrogen sulphide method applied to pure iron in the presence of up to 25 mg. of vanadium confirmed the absence of effect on the iron titre. The reactions before the hydrogen sulphide treatment ensure the presence of pentavalent vanadium; hydrogen sulphide reduces this to the tetravalent condition which is not affected by the dichromate titration. The use of potassium permanganate in place of dichromate would, of course, effect reoxidation of the tetravalent vanadium and yield erroneous iron values.

Molybdenum—Complete precipitation of molybdenum sulphide is difficult, as hydrogen sulphide tends to produce some reduced Mo which escapes precipitation. Thus, although the effect of Mo is not marked and its complete elimination is not essential, tests have been carried out to determine suitable precipitation conditions. The results are summarized below:

(i) Temperature of precipitation varying between 20° and 100° C. has no significant effect

(ii) Lower acid concentrations yield more complete precipitation of molybdenum sulphide, but greater possibility of co-precipitation of iron sulphide

(iii) Fast rates of hydrogen sulphide flow give more complete precipitation.

No single treatment has been found to give complete precipitation of molybdenum sulphide, and invariably a further small precipitate forms in the filtrate during boiling to remove hydrogen sulphide. Although this further precipitation does not complete the separation of Mo, the subsequent iron titres are not seriously affected and are unlikely to be high by more than 0·2 ml. of $N/10$ potassium dichromate. For most routine purposes, therefore, the single precipitation suffices, but for extremely accurate work it is preferable to complete the removal of Mo by a second precipitation. The second precipitation is effected in the filtrate after boiling to remove hydrogen sulphide, by treating with a little potassium permanganate to oxidize the residual Mo and again passing hydrogen sulphide under the recommended conditions.

Acid Radicals—The hydrogen sulphide method should normally be operated in dilute sulphuric acid; if other mineral acids, *e.g.*, nitric or hydrochloric acid, have been used in decomposing any particular sample, they should be eliminated by evaporating the solution to fumes of sulphuric acid (or of perchloric acid) before the hydrogen sulphide reduction. The method can be operated successfully in the presence of perchloric acid or boric acid.

Major amounts of phosphoric acid or hydrofluoric acid have a marked effect on the reduction of ferric iron by hydrogen sulphide, leading to low results (*see* p. 396). It would appear that the weakly ionizable ferric phosphate and fluoride are incompletely reduced by hydrogen sulphide. Furthermore, there is a danger of extraneous iron contamination if the hydrofluoric acid treatment is carried out in glassware. Thus phosphoric acid as a solvent is not permissible; hydrofluoric acid may be used provided that the decomposition does not introduce extraneous iron and the excess hydrofluoric acid is eliminated by heating to fumes of sulphuric or perchloric acid before the ferric iron reduction stage.

Final Trial on Pure Iron Samples

The fundamental reproducibility of the hydrogen sulphide method is illustrated by the following results on a pure iron sample:

0·5-*g. Sample, B.C.S.* '*A2*'

Laboratory	$N/10$ Dichromate, ml. (Individual Values)
1	89·2, 89·2
2	89·2, 89·1, 89·2, 89·0, 89·3
3	89·1, 89·2, 89·05, 89·1, 89·25
Average	89·15
Range	± 0·15

The total range of 12 determinations from three laboratories is thus 89·0–89·3 ml. of $N/10$ potassium dichromate.

DETERMINATION OF IRON IN MISCELLANEOUS SAMPLES

Trials carried out on a wide variety of substances have shown that different procedures are needed to obtain complete decomposition of these materials; considerable activity has been directed to this aspect of the iron determination and the practical importance of certain other features has been revealed.

Condition of Sample for Analysis

It is suggested that the analysis sample as received should be crushed in an agate or other suitable mortar, avoiding extraneous contamination, to pass a British Standard 85-mesh sieve and dried at 105° C. to constant weight. This treatment is generally satisfactory, but certain materials, *e.g.*, Sproxton iron ore, rehydrate so rapidly that satisfactory weighing of the sample is most difficult. This point is clearly of importance in accurate analysis and the following treatment has been recommended as being most generally satisfactory:

> The iron determination shall be applied to samples in the 'dried at 105° C. to constant weight' condition, but where rapid rehydration occurs the laboratory sample shall be 'air-dried,' *i.e.*, exposed to the laboratory atmosphere until a stable condition with respect to moisture is obtained. The time required will vary according to the type and origin of the sample, and unknown samples should be weighed at intervals until constant weight is obtained. From this air-dried sample two portions shall be weighed, one for the iron test and the other for the determination of moisture by B.S.I. method 1016: part 2*C*(i). The titre obtained in the iron test shall then be corrected to a moisture-free condition on the basis of the companion moisture test. If at a later date a repeat iron test is required, a companion moisture test shall also be carried out.

Decomposition Procedures

It is not possible to deal adequately in this report with this aspect of the analysis of oxide-type substances, and as it is undergoing examination on a broader basis a more detailed report will be made available later. Therefore, it is proposed only to give general considerations and to indicate those procedures that have been found satisfactory.

General Considerations

The success of a particular decomposition procedure may depend entirely on the state of division of the

sample. For fusion procedures, samples should be finely ground in an agate, sintered-carbide, or sapphire mortar, but care should be exercised, particularly with an agate mortar, to avoid contaminating the sample by excessive grinding.

Blank effects arising from extraneous iron or interfering elements in the reagents or apparatus used for the decomposition should be minimized; glassware used for iron determination should be specially cleaned by boiling hydrochloric acid. Platinum interference should always be suspected if Pt crucibles are used in the decomposition of the sample. Special care should be taken to ensure that the use of hydrofluoric acid in a glass beaker to assist mineral acid decomposition of a sample does not introduce extraneous iron. Similarly, Ni crucibles, sodium peroxide, and technical grades of perchloric acid are frequent sources of extraneous iron blanks.

Solvent or flux should be chosen with care. Interfering acids, *e.g.*, phosphoric, must be avoided; sulphuric acid should not be used in the decomposition of basic slag or other lime-rich substances, and fluxes containing potassium should not be used in a method involving perchloric acid.

The most satisfactory method of decomposing samples for the determination of iron is by acid attack; most iron- and steelmaking raw materials, slags, and refractories, which contain sufficient iron to warrant a volumetric determination, are largely soluble in some mineral acid or mixture of acids. Even samples containing a substantial proportion of acid-insoluble constituents are best given a preliminary acid treatment as this reduces the amount of material requiring decomposition by other means. In all work of high accuracy the insoluble residue from the preliminary acid attack should be subjected to a further decomposition, for which bisulphate fusion in a silica crucible is generally satisfactory.

Special Recommendations

Iron ores, sinters, tap cinders, mill scale, or Mn ores are generally soluble in acids. The more highly siliceous materials, particularly the sinters and tap cinders, may require the addition of a few drops of hydrofluoric acid or a somewhat longer digestion period. A little stannous chloride often assists the decomposition of these materials.

The addition of a little sulphurous acid is of assistance in the decomposition of the manganese ores. With these substances decomposition of the iron-bearing constituents is generally complete in the acid attack and only in exceptional cases is there an insoluble residue which requires further treatment.

Blast-furnace slags and basic steelmaking slags are generally soluble in acids. Sulphuric acid should not be used and for the hydrogen sulphide method (Appendix II) perchloric acid is most satisfactory. Acid decomposition of these lime-rich substances is assisted by initial boiling with a little water, followed by slow addition of the acid.

Silica-base refractories, acid slags, bauxite, and natural clays are most conveniently decomposed by treatment with sulphuric, hydrofluoric, and nitric acids in a Pt dish. Hydrofluoric and nitric acids should be eliminated before proceeding with the iron determination. Any insoluble matter remaining will be substantially free of iron, but if complete decomposition is required, the residue should be fused with sodium carbonate or bisulphate.

The most effective decomposition of chrome ores and chrome-magnesite refractories is by fusing with sodium peroxide. Unfortunately, this reagent and the Ni crucibles in which the fusion is generally carried out contain iron, and correction for such errors is impracticable, as it must take into account the amount of peroxide used and the composition and loss of weight of the crucible. With careful temperature control the sodium peroxide fusion can be effected in other crucibles, *e.g.*, silica, porcelain, or Pt previously lined with sodium carbonate, thereby eliminating one source of iron blank, but such procedures are

Table IX

FINAL TRIALS OF HYDROGEN SULPHIDE METHOD ON IRON-ORE SAMPLES

Iron, %

Laboratory	MGS/80	MGS/81	MGS/82	MGS/83	MGS/84	MGS/85	MGS/86	MGS/87	MGS/88	BCS/244	BCS/245	BCS/175
	Kiruna	Cleveland	Djerissa	Sproxton	Lincolnshire	Hematite	Mysur-Orne	Sierra Leone	Wabana	Magnetite	Hematite	Standard Iron Ore
1	65·1	30·5	57·4	41·9	24·8	40·05	43·7	56·8	52·6	56·0	33·75	58·15
2	65·3	30·4	57·3	41·9	24·8	39·9	43·5	56·8	52·5	55·55	33·65	58·0
3	65·5	30·5	57·3	41·85	24·9	40·05	43·65	57·0	52·45	56·05	34·0	58·25
4	65·3	...	57·2	42·0	...	...	...	56·9	...	55·75	33·85	58·15
5	65·45	30·55	57·2	42·05	25·0	40·1	43·7	57·0	52·55	55·75	34·05	58·05
6	65·25	30·55	57·15	41·75	24·75	40·15	43·75	56·5	52·4	55·8	33·85	58·0
7	65·55	30·6	57·3	41·9	24·85	40·2	43·75	56·95	52·5	55·8	33·7	58·05
8	65·3	30·4	57·0	41·55	24·7	40·3	43·6	56·5	52·3	55·7	33·6	58·0
9	...	...	57·0	41·7	...	40·1	43·55	56·7	52·5	55·7	33·8	...
10	65·5	30·45	57·1	41·9	25·15	39·8	43·55	56·85	52·5	55·7	33·65	57·9
11	65·1	30·5	57·1	41·75	24·65	40·0	43·6	56·5	52·5	56·0	34·1	58·15
12	65·3	30·35	57·2	42·0	24·75	39·9	43·45	57·0	52·5	55·95	33·85	58·2
Average	65·3	30·5	57·2	41·85	24·85	40·05	43·6	56·8	52·5	55·8	33·8	58·1
Deviation +	0·25	0·1	0·2	0·2	0·3	0·25	0·15	0·2	0·1	0·25	0·3	0·15
Deviation −	0·2	0·15	0·2	0·3	0·2	0·25	0·15	0·3	0·2	0·25	0·2	0·2

Table X

FINAL TRIALS OF HYDROGEN SULPHIDE METHOD ON MISCELLANEOUS SAMPLES
Iron, %

Laboratory	MGS/147	MGS/100	MGS/101	MGS/102	MGS/103	MGS/104	MGS/105	MGS/106	MGS/107	MGS/108	MGS/129	MGS/139
	Basic Slag	Basic Slag (F-Bearing)	Basic Slag	Acid Slag	Aluminous Clay	Manganese Ore	Chromite	Chrome-Magnesite Brick	Tap Cinder	Sinter	Bauxite	Turkish Chromite
1	8·65	7·35	11·55	6·15	7·2	15·05	18·1	8·05	49·55	42·7	15·7	11·1
2	8·7	7·35	11·55	6·1	7·0	14·95	18·1	8·0	49·35	42·7	15·7	11·2
3	8·7	7·25	11·45	6·15	7·05	15·0	18·05	7·9	49·4	42·55	15·75	11·15
4	8·7	7·3	11·45	6·15	7·1	14·95	18·05	8·15	49·45	42·5	15·7	11·2
5	8·85	7·35	11·5	6·05	6·95	14·9	18·0	8·15	49·5	42·75	15·75	11·15
6	8·65	7·3	11·35	6·1	7·0	14·95	17·95	7·8	49·3	42·75	15·7	11·15
7	8·7	7·4	11·5	6·15	7·0	15·0	18·0	7·9	49·55	42·5	15·7	11·35
8	8·9	7·4	11·5	6·15	7·05	15·1	17·95	8·3	49·5	42·7	15·8	11·5
9	...	7·4	11·6	6·1	7·1	15·0	18·1	8·1	49·7	42·5	...	...
10	8·8	7·3	11·4	6·1	6·95	14·9	17·9	7·9	49·25	42·8	15·85	11·2
11	8·75	7·25	11·6	6·05	...	15·0	18·1	8·1	49·5	42·65	...	...
12	8·75	7·25	11·5	6·2	7·15	14·95	...	7·95	49·4	42·65	15·85	11·4
13	8·7											
Average	8·75	7·35	11·5	6·1	7·05	15·0	18·0	8·05	49·45	42·65	15·75	11·25
Deviation +	0·15	0·05	0·1	0·1	0·15	0·1	0·1	0·25	0·25	0·15	0·1	0·25
Deviation −	0·1	0·1	0·15	0·05	0·15	0·1	0·1	0·25	0·2	0·15	0·05	0·15

so critical that their general use cannot as yet be recommended.

Attack by hydrochloric and nitric acids, followed by perchloric acid and evaporation to fumes, provides a satisfactory alternative for these chrome-bearing refractories. No extraneous iron is introduced and although Cr interference in the subsequent iron determination is not serious this method of treatment permits of its elimination as the volatile chromyl chloride. With certain chrome ores this form of decomposition may be somewhat lengthy, but it is hastened by fine comminution of the sample. In such cases, acid attack should not be prolonged but the insoluble residue should be removed for a separate fusion treatment.

Results of Final Trials

The results obtained in final trials of the two methods for iron on a wide variety of substances are given in Tables VI, VII, IX, and X. The decomposition procedures used by the co-operators for a particular sample were not identical, but were in accordance with the foregoing general principles.

SUMMARY AND CONCLUSIONS

Two volumetric methods for the determination of iron when present in ores, slags, refractories, and other oxide-type materials as major constituent have been critically examined and their scope and limitations are defined.

One method makes use of stannous chloride and the other hydrogen sulphide for the reduction of ferric to ferrous iron. Both methods conclude with a dichromate titration of the ferrous iron, using diphenylamine sulphonate as internal indicator.

Table XI

SUMMARY OF RESULTS OF VOLUMETRIC AND ABSORPTIOMETRIC DETERMINATIONS
Iron, %

Laboratory	MGS/40A		MGS/152		MGS/153	
	Volumetric	Absorptiometric	Volumetric	Absorptiometric	Volumetric	Absorptiometric
1	...	0·195	...	0·385	...	0·43
2	0·205	0·195	0·425	0·38	0·475	0·425
3	0·215	0·205	0·40	0·405	0·44	0·445
4	0·21	...	0·395	...	0·445	...
5	0·22	0·235	0·41	0·38	0·44	0·42
6	0·205	0·20	0·39	0·40	0·44	0·445
7	0·20	0·23	0·39	0·39	0·45	0·46
8	0·21	0·225	0·395	0·40	0·44	0·45
9	0·22	0·22	0·41	...	0·455	...
10	0·205	0·22	0·40	0·40	0·445	0·425
11	0·22	0·22	0·39	0·38	0·45	0·46
Average	0·21	0·215	0·40	0·39	0·45	0·44
Range	0·02	0·04	0·035	0·02	0·035	0·04

The stannous chloride reduction method gives erroneous results in the presence of Pt, Mo, Cu, V, and large amounts of phosphate or nitrate.

The hydrogen sulphide method is not subject to interference from other metals, but is affected by large amounts of phosphate, nitrate, fluoride, or chloride. The latter three acid radicals are easily removed by evaporating to fumes of sulphuric or perchloric acid before the reduction, but phosphoric acid must not be used in the initial solvent and may only be added after the reduction of the ferric iron.

Hydrofluoric acid, if used to assist decomposition of samples in glass vessels, can give rise to serious iron contamination from the glassware.

The methods, detailed in Appendices I and II, have been applied to a wide variety of iron- and steelworks raw materials, refractories, and products. The results obtained are reported and certain recommendations are made regarding methods of decomposition of the various materials.

Part II—DETERMINATION OF IRON BELOW 3%

Volumetric Method

In view of its greater freedom from interferences, the hydrogen sulphide method only was selected for examination. The following modifications were made to achieve greater precision:

(*a*) Larger sample weight, 2 g.
(*b*) Weaker standard titrant, *N*/50
(*c*) Preoxidized diphenylamine indicator to reduce blank effects.

Absorptiometric Method

The absorptiometric method (Appendix III) is based on the colour reaction of ferrous iron with thioglycollic acid in ammoniacal citrate solution, the reagent serving both to reduce ferric iron and to colorize the resulting ferrous iron.

Samples Examined

The two methods have been applied to three samples:

(*a*) A blast-furnace slag, *MGS*/40*A*
(*b*) A silica brick, *MGS*/152
(*c*) A sillimanite brick, *MGS*/153.

As no single specified decomposition procedure would be equally satisfactory for all three materials, different decomposition procedures and subsequent treatments were used to obtain complete decomposition and to yield test solutions suitable for each method, *viz.*, for the volumetric method either a sulphuric acid or a perchloric acid solution, and for the absorptiometric method a sulphuric acid solution. The study of decomposition procedures in relation to types of sample has been treated briefly in Part I.

For general purposes, however, an acid attack, including hydrofluoric acid, followed by evaporation to fumes of sulphuric or perchloric acids and by fusion of any remaining insoluble matter, should be applicable to most oxide materials of low iron content. The results (averages of two or more results) obtained are given in Table XI.

Discussion

The results obtained by the two methods are satisfactory, and it is clear that both are suitable for these low iron contents. In practice, however, the two methods are likely to find different fields of application.

The present work shows that the lower limit of the volumetric method for major contents of iron can be extended to cover iron contents below 1% with commendable accuracy. It is proposed that when the hydrogen sulphide method (Appendix II) is submitted to the British Standards Institution as a standard procedure, its range should be extended to include these lower iron levels by the special reference in Note 1. The absorptiometric method will also be recommended as an alternative for this range.

APPENDIX I

Stannous Chloride Method

Solutions Required

Stannous Chloride (10%)—Dissolve 10 g. of stannous chloride ($SnCl_2.2H_2O$) in 50 ml. of hydrochloric acid (sp. gr. 1·16), dilute to 100 ml., and mix. *N.B.*—This solution must be freshly prepared.

Mercuric Chloride (4%)—Dissolve 4 g. of mercuric chloride in 80 ml. of hot water, cool, dilute to 100 ml., and mix.

Phosphoric–Sulphuric Acid (3: 3: 14)—To 600 ml. of water add cautiously with stirring 150 ml. of phosphoric acid (sp. gr. 1·75) and 150 ml. of sulphuric acid (sp. gr. 1·84), cool, dilute to 1 litre, and mix.

Diphenylamine Sulphonate Indicator—(*a*) Unoxidized barium diphenylamine sulphonate. Dissolve 0·32 g. of barium diphenylamine sulphonate in hot water, cool, dilute to 100 ml., and mix. (*b*) Preoxidized sodium diphenylamine sulphonate (for work of highest accuracy). *See* footnote to Table IV.

Potassium Dichromate (*Decinormal*) — Dissolve 4·9035 g. of potassium dichromate (previously crushed, dried at 180° C., and cooled in a desiccator) in water, dilute to 1 litre, and shake well. 1 ml. of this solution at 20° C. = 0·005585 g. of iron.

Procedure

Decompose 0·500 g. of sample (*see* Note 1) by heating with 25 ml. of hydrochloric acid (sp. gr. 1·16) (Note 2). Add 0·1 g. of potassium chlorate crystals, boil for 2 min., rinse the inner walls of the flask with water, and boil to expel chlorine (Note 3).

Dilute to about 50 ml. and boil. Add stannous chloride solution (10%) dropwise until the yellow colour is just discharged, followed by a further 3 drops excess. Cool and dilute to 100 ml. with freshly boiled and cooled water.

Add 12 ml. of mercuric chloride solution (4%) and allow to stand for 2–3 min. (low results may be obtained if this time limit is exceeded).

Add 20 ml. of phosphoric–sulphuric acid and 5 drops of barium diphenylamine sulphonate indicator (Note 4). Dilute to 300 ml. and titrate with *N*/10 potassium dichromate until one drop changes the colour of the solution from green to purple (Note 5).

Notes

(1) Over the range 5–100% of iron, reproducibility in the absence of interfering elements is ± 0·15%

of iron. By increasing the sample weight, using $N/50$ standard dichromate and the preoxidized indicator, better reproducibility can be achieved in the lower iron ranges and reliable results may be obtained down to 0·3% of iron; poorly soluble materials requiring a special decomposition may not be within these reproducibility limits.

Results will be inaccurate if the following elements are present in the test solution in amounts greater than: Pt 0·25 mg., V 1 mg., Cu 2·5 mg., Mo 2 mg.

For samples outside these ranges, the hydrogen sulphide method (*see* Appendix II) should be used.

The laboratory sample shall be ground and dried with suitable precautions (*see* p. 398).

(2) Basic slag and blast-furnace slag samples should first be boiled with water and the hydrochloric acid then added slowly, to prevent coagulation of the sample into globules resistant to attack.

Decomposition by hydrochloric acid is satisfactory for most types of iron ore, scale, sinter, blast-furnace and basic slag. The decomposition of less soluble materials is facilitated by:

(i) 0·5 ml. of hydrofluoric acid, care being taken to avoid iron contamination from the glassware
(ii) Reduction with excess stannous chloride and prolonged digestion.

The decomposition of Mn ores is assisted by the addition of a little sulphurous acid.

Silica-base refractories, acid slags, bauxite, and silicate minerals are best decomposed by treatment with sulphuric, nitric, and hydrofluoric acids in a Pt dish, and evaporation to fumes.

Chrome ores and chrome-magnesite refractories may be decomposed as follows:

Treat 0·5 g. of finely divided sample with 15 ml. of hydrochloric acid (sp. gr. 1·16) and 5 ml. of nitric acid (sp. gr. 1·42) and digest at boiling point for 10 min. (The decomposition is sometimes assisted by the presence of 5–10 ml. of sulphuric acid (sp. gr. 1·84) in the initial solvent. This modification is not of general application and should not be used in the presence of large amounts of Ba or Ca.) Cool, add 20 ml. of perchloric acid, and evaporate to fumes. Fume strongly for 5 min. with the beaker covered by a watch glass.

If Cr is to be removed, treat the fuming solution with a few drops of hydrochloric acid and again fume. Repeat the addition of drops of hydrochloric acid followed by fuming until no further evolution of chromyl chloride occurs.

Cool, dilute with water, filter, and if necessary treat the insoluble residue by fusion with sodium bisulphate in a silica crucible.

Other possible alternatives include sodium peroxide fusion in Ni crucibles, or in silica or Pt crucibles lined with sodium carbonate, but in all such decompositions extraneous iron may be introduced.

With the foregoing alternative treatments for silica-base refractories and for chrome ores, etc., the subsequent addition of potassium chlorate is unnecessary.

(3) For general work white silica residues may be safely ignored, but any coloured residues should be removed and treated as follows:

Filter the solution through a paper pad, washing with dilute hydrochloric acid (1: 19), and ignite the residue in a Pt crucible. To the cooled crucible add a little water, 1 ml. of hydrofluoric acid, and evaporate to dryness. Take up in 2 ml. of hydrochloric acid (sp. gr. 1·16), dilute, and add to the main filtrate.

If the decomposition is still not complete collect the residue on a paper pulp pad, ignite in a silica crucible, and fuse with 1–2 g. of sodium bisulphate, extracting in the original solution.

Where decomposition involves the use of Pt crucibles, contamination with Pt may occur and use of the hydrogen sulphide method (Appendix II) is advisable.

(4) Five drops of this indicator give a blank of approximately 0·05 ml. of $N/10$ potassium dichromate.

(5) The volume of titrant used should be corrected for any temperature difference between the titrant and burette calibration temperature.

APPENDIX II

Hydrogen Sulphide Method

Solutions Required

Dilute sulphuric acid (1: 9).

Potassium permanganate (0·5%).

Acid Sulphide Wash—To 900 ml. of water, add 20 ml. of sulphuric acid (sp. gr. 1·84), cool, dilute to 1 litre, mix, and pass a rapid stream of hydrogen sulphide gas for not less than 10 min.

Dilute sulphuric acid (1: 1).

Diphenylamine Sulphonate Indicator—(*a*) Unoxidized barium diphenylamine sulphonate (*see* Appendix I). (*b*) Preoxidized sodium diphenylamine sulphonate (*see* Appendix I).

Potassium dichromate (decinormal) (*see* Appendix I).

Procedure

Decompose 0·500 g. of sample (*see* Note 1) by heating with 25 ml. of hydrochloric acid (sp. gr. 1·16) (Note 2). Add 10 ml. of dilute sulphuric acid (1: 1), evaporate to fumes, cool, dilute to about 110 ml. Heat to boiling, oxidize with dropwise additions of potassium permanganate solution (0·5%) until the solution is just pink, and add 0·5 ml. excess. Boil to destroy carbonaceous matter, adding more potassium permanganate solution if necessary (Note 3). Dilute to approximately 350 ml., heat the solution to boiling, remove from the hot plate, and pass a rapid stream of hydrogen sulphide gas through the solution for 15 min. (Note 4).

Digest the solution at 60° C. for 15 min. and filter through a paper pulp pad, washing with acid sulphide wash (Note 5). Add 10 ml. of dilute sulphuric acid (1: 1) to the filtrate and boil until free from hydrogen sulphide (test with a lead acetate paper, 10 min. usually suffices), and continue boiling vigorously for a further 10 min. Cool, add 5 ml. of phosphoric acid (sp. gr. 1·75), 5 drops of barium diphenylamine sulphonate, and titrate with $N/10$ potassium dichromate until one drop changes the colour of the solution from green to purple. *See* Appendix I, Note 5.

Notes

(1) *See* Appendix I. A reproducibility of $\pm$ 0·02% of iron may be obtained in the range 0·05–2·0% of iron by the following modification (*see* Part II):

Transfer 2 g. of sample to a Pt crucible or dish, add 20 ml. of hydrochloric acid (sp. gr. 1·16) and 10 ml. of hydrofluoric acid, and digest for 15 min. Add a further 10 ml. of hydrofluoric acid, digest for 5 min., and cool. Add 5 ml. of sulphuric acid (sp. gr. 1·84), evaporate to fumes, and cool. Dilute with about 25 ml. of water, digest for 30 min., and filter on a paper pad, washing well and receiving the filtrate in a 400-ml. beaker.

Return the pad and residue to the Pt vessel, char the paper, and ignite at 900° C. Add 1 g. of potassium bisulphate, fuse, cool, and extract into the previous filtrate.

Dilute to approximately 350 ml. and continue the analysis as under ' Procedure,' performing the titration with *N*/50 potassium dichromate solution and pre-oxidized barium diphenylamine sulphonate indicator.

For iron contents of 2·0–5·0%, a 1-g. sample and half quantities of hydrochloric and hydrofluoric acids may be used, when a reproducibility of ± 0·05% of iron should be achieved. A blank determination should be carried out on corresponding quantities of all reagents used.

Other metals do not interfere in this method. Fluorides, nitrates, or nitric acid used in the initial decomposition are removed by subsequent fuming. The use of phosphoric acid at any stage before the sulphide reduction is not permissible as the phosphate ion retards the reduction of ferric iron.

(2) The method of decomposition must be adjusted to suit the substance being examined. If the substance is soluble in dilute sulphuric acid, the preliminary treatment with hydrochloric acid is unnecessary. In general, however, the procedures outlined in Notes 2 and 3 of Appendix I are applicable, except that the stannous chloride should not be used as an aid to hydrochloric acid decompositions. When complete decomposition has been obtained the solution conditions must be adjusted to provide a dilute sulphuric acid solution before the hydrogen sulphide stage. For samples containing high contents of Ca, perchloric acid should be substituted for sulphuric acid.

(3) If an oxidizing form of decomposition has been used, the treatment with potassium permanganate is unnecessary and should be omitted.

(4) The hydrogen sulphide generator should be capable of maintaining a consistent gas flow of at least 1 litre/min.; a ' bubble ' delivery tube should be used to facilitate rapid saturation of the test solution. A trap to prevent transfer of iron salts into the test solution must be included in the system, *e.g.*, 200 ml. of water contained in a 1000-ml. conical flask with delivery tube extending almost to the bottom of the flask and outlet tube projecting only about ¼ in. below the underside of the bung. The flask should be rinsed out and charged with fresh water before each batch of determinations.

Tungsten, if present, may be partly hydrolysed and removed with the sulphide precipitate. Any tungsten remaining in solution has no effect on the titration.

(5) If a considerable precipitate is obtained, adsorption of iron may occur. The pad and precipitate should then be ignited, dissolved in nitric acid, fumed with sulphuric acid, and the sulphides reprecipitated as before. The filtrate may then be added to the main solution.

With samples containing large amounts of Mo, separation of this element may not be complete. Any Mo remaining in solution may be removed as follows:

Boil the filtrate free from hydrogen sulphide, add 5 ml. of potassium permanganate solution (0·5%), and remove from the hot plate. Repeat the hydrogen sulphide treatment as described above, filtering off and washing any further molybdenum sulphide obtained. Proceed with the determination exactly as described above.

APPENDIX III

Absorptiometric Method

Special Apparatus Required

This procedure may be carried out with the Hilger Photoelectric Absorptiometer or a similar instrument. With the former, the following accessories are required: Mercury vapour lamp, Ilford No. 605 and Calorex No. H.503 filters, 2- or 4-cm. cells.

Replicate determinations should not differ by more than ± 0·01% below 0·2% (0·01–0·2% iron) or ± 0·02% above 0·2% (0·2–1·0% iron).

Solutions Required

Citric acid (20%). Ammonium hydroxide (1: 1).
Thioglycollic acid (1: 9). Sulphuric acid (1: 9).

Procedure

Treat a 0·5-g. sample as described in the first two paragraphs of Note 1, Appendix II, receiving the filtrate in a 250-ml. graduated flask.

Proceed by diluting the filtrate to 250 ml., shaking well, and pipetting 20 ml. (40 ml. for iron contents below 0·2%) into a 50-ml. graduated flask. Add 2 ml. of citric acid (20%), 1 ml. of thioglycollic acid (1·9), and 6 ml. of ammonium hydroxide (1: 1), dilute to the mark, and mix well.

Stand for 10 min. and measure the absorption of the solution.

Calibration

Standard Iron Solution—Dissolve 0·7021 g. of ferrous ammonium sulphate ($FeSO_4.(NH_4)_2SO_4.6H_2O$) in water and dilute to 1 litre. 1 ml. of the solution contains 0·0001 g. of iron.

Dilute Iron Solution—Dilute 200 ml. of the standard iron solution to 1 litre. 1 ml. of this solution contains 0·00002 g. of iron.

Procedure—Deliver into 50-ml. flasks suitable volumes of the iron solutions to cover the range required, dilute each to about 20 ml., add 10 ml. of sulphuric acid (1: 9) and treat as under ' Procedure.' Construct calibration graphs from the readings obtained.

Phosphorus–Oxygen Equilibria in Liquid Iron

By J. B. Bookey, F. D. Richardson, and A. J. E. Welch

SYNOPSIS

The thermodynamics of the phosphorus–oxygen equilibrium in liquid iron have been studied by bringing the phosphorus content of liquid iron to equilibrium with a mixture of tetracalcium phosphate ($Ca_4P_2O_9$) and calcium oxide, and a controlled gas atmosphere of water vapour and hydrogen. The iron was heated by induction in a crucible made from the mixture of phosphate and lime. The phosphorus content of the iron under these conditions depends only on the temperature and on the oxygen potential of the gas phase. Studies have been made at 1540°, 1560°, and 1580° C., with a tenfold range of oxygen potentials, and covering 0·008–1% of phosphorus in the iron. The results have been interpreted in terms of interaction between phosphorus and oxygen dissolved in liquid iron, and lead to a value of the standard free-energy change for the reaction

$$2[P]\ (\text{in iron}) + 5[O]\ (\text{in iron}) + 4CaO\ (\text{solid}) \rightleftharpoons Ca_4P_2O_9\ (\text{solid})$$

A similar reaction has been studied in pure lime crucibles. In this case, the iron phase can only lose phosphorus to the lime. The results, when the effect of the presence of small amounts of silicon has been taken into account, agree with those outlined above.

Introduction

THE importance of phosphorus elimination in the manufacture of steel has led to numerous investigations of the equilibria between liquid iron, containing dissolved phosphorus, and slags of different types. In many instances, the phosphorus contents of metal and slag from actual heats in basic open-hearth furnaces have been determined, and attempts have been made to correlate the phosphorus distribution with slag composition, temperature, and other relevant variables. Such studies may provide a useful empirical guide to desirable conditions of furnace operation in the works, but, at the present stage in the development of steelmaking chemistry, they yield little fundamental information of a quantitative character. The phosphorus-containing slags obtained in a steel furnace are complex in constitution, and means are not yet available for accurate estimation of the activities of their components ; moreover, true equilibrium between slag and metal may not be attained under works conditions. The extensive work of Schenck and Riess[10] on heats in basic open-hearth and Bessemer furnaces is typical of many attempts to obtain fundamental information from unduly complex systems. Winkler and Chipman,[11] although working in the laboratory with equipment that allows closer control of experimental conditions, have also used relatively complex slag systems. There is therefore an evident need for phosphorus-equilibrium studies in systems sufficiently simple for direct thermodynamic interpretation of the results.

Basic thermodynamic data (specific heats, standard free-energy changes, and heats of reaction or solution), from a variety of sources, have been used by Richardson and Jeffes[9] to derive values of the standard free-energy change ($\Delta G°$) for the reaction

$$2[P] + 2\tfrac{1}{2}O_2\ (\text{gas}) + 3CaO\ (\text{solid}) \rightleftharpoons Ca_3P_2O_8\ (\text{solid}).$$

(Here and elsewhere in this paper the use of square brackets denotes dissolved constituents of the liquid-iron phase.) The results could at once be used to compute equilibrium phosphorus concentrations in liquid iron in contact with solid $Ca_3P_2O_8$ and lime, at specified oxygen pressures ; unfortunately, however, the phosphate $Ca_3P_2O_8$ (tricalcium phosphate) does not occur in equilibrium with lime at steelmaking temperatures, and corresponding data are not yet available for the appropriate phosphate phase, which is tetracalcium phosphate, $Ca_4P_2O_9$. Apart from this limitation, the data of Richardson and Jeffes are subject to considerable error on account of indirect derivation from somewhat inaccurate information.

The present paper describes a series of measurements of the phosphorus–oxygen equilibria in liquid iron in contact with tetracalcium phosphate and lime, probably the simplest system in which phosphorus equilibria of steelmaking interest can be studied. The reaction underlying the measurements is :

$$2[P] + 5[O] + 4CaO\ (\text{solid}) \rightleftharpoons Ca_4P_2O_9\ (\text{solid}) \quad \ldots(1)$$

The phase diagram[3] for the system $CaO–P_2O_5$ indicates slight solid solubility (about 4% CaO) of lime in $Ca_4P_2O_9$, but at a fixed temperature below the $CaO–Ca_4P_2O_9$ eutectic the activities of lime and of lime-saturated tetracalcium phosphate will be constant ; the dissolved phosphorus activity ($a_{[P]}$) will therefore depend only on the oxygen activity ($a_{[O]}$) in the metal, to which it should be related by the expression :

$$\frac{1}{a^2_{[P]} \cdot a^5_{[O]}} = K_1 \quad \ldots(1a)$$

In the experiments described in this paper, liquid iron containing phosphorus, at a known temperature,

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was allowed to react with a mixture of lime and tetracalcium phosphate in the presence of a controlled atmosphere of hydrogen and water vapour. This atmosphere established a known equilibrium oxygen activity in the iron melt, thus fixing the $a_{[O]}$ term in equation (1*a*). The corresponding equilibrium phosphorus content in the melt was assessed by observing the direction and extent of transfer of phosphorus (by reaction (1)) between the metal and the lime–phosphate phase. Two series of measurements were carried out; in the first, iron (containing some phosphorus) was heated in a crucible lined with a mixture of lime and tetracalcium phosphate, and, by subsequent analysis, transfer of phosphorus to or from the iron melt could be established. The second series employed pure lime crucibles and a phosphorus-containing melt; oxidation of phosphorus then led to formation of tetracalcium phosphate at the lime surface, phosphorus transfer being possible only from the metal to the crucible. The second series of measurements revealed that in the presence of sufficient silicon or silica, a calcium silico-phosphate is formed in preference to tetracalcium phosphate.

EXPERIMENTAL TECHNIQUES

Materials

Tetracalcium Phosphate—Tetracalcium phosphate was prepared from a mixture of the requisite proportions of calcium carbonate and di-ammonium hydrogen phosphate, which was heated slowly to 1000° C. in a platinum basin; heating was continued until the product was constant in weight. The starting materials were of 'AnalaR' grade. A small excess of the calcium carbonate was deliberately introduced so that the product contained some lime rather than tricalcium phosphate. An X-ray powder photograph of the material showed close agreement with the data of Bredig,[2] except that one strong line reported by Bredig (lattice spacing $d = 2{\cdot}99$ Å.), and now believed to be spurious, was not observed.

Iron—The following impurity contents have been recorded for the iron used in equilibrium measurements: 0·02% C, 0·005% Si, 0·005% Mn, 0·006% S, 0·002% P, 0·08% Ni, 0·0035% Cr, 0·002% Mo, 0·005% Co, and 0·01% Cu. The iron used for the phosphorus master alloy was a Swedish pure iron with the following analysis: 0·05% C, 0·02% Si, $<$0·005% Mn, 0·015% S, 0·001% P, 0·01% Ni, $<$0·01% Cr, $<$0·01% Mo, $<$0·02% W, $<$0·01% V, $<$0·02% Ti, $<$0·01% Co, $<$0·01% Cu, $<$0·005% Al, $<$0·02% Sn.

Iron–Phosphorus Master Alloys—The preparation of iron–phosphorus alloys of predetermined composition was simplified by the use of a master alloy, usually containing 1–2% of phosphorus. This was prepared by addition of red phosphorus to molten iron, in the apparatus shown in Fig. 1*a*.

Iron, contained in a sintered alumina crucible *A*, was induction-melted by means of the high-frequency coupling coil *B* connected to a suitable generator (*see* below). During heating, hydrogen was passed through the silica outer tube, but nitrogen was substituted as soon as the iron had melted. The prism, which allowed convenient observation of the melting process, was then replaced by a bung, and the release slide *C* was pushed in, thereby blocking the vertical tube. A small pellet of red phosphorus was introduced by removing the bung, which was quickly replaced, and the pellet was allowed to drop into the iron by manipulation of the release slide. Reaction proceeded smoothly, and, after suitable intervals, further phosphorus pellets were added. Some phosphorus vapour escaped with the nitrogen, and was led away into a fume cupboard; a little phosphorus also condensed, in the yellow form, on cooler parts of the apparatus, so that particular care was necessary in the dismantling of the cold tube.

Cooling of the master alloy in the crucible, inside the apparatus, led to inhomogeneity in the product, in spite of the quite rapid cooling allowed by the use of induction heating (*e.g.*, opposite sides of a typical ingot contained 1·57% and 1·79% of phosphorus). The alloy was therefore remelted and the melt quenched by a special technique. The remelting was carried out in hydrogen in a similar apparatus, and the temperature of the melt was adjusted to 1650° C. A rapid current of nitrogen was then passed into the silica outer tube, and allowed to escape through the open top end *D* of the vertical central tube. A long, thin-walled silica tube, of about 2 mm. dia., was lowered through *D* until its lower end dipped into the melt, and, by judicious application (through a stopcock) of suction from a filter pump, a quantity of molten metal was sucked up into the tube. It

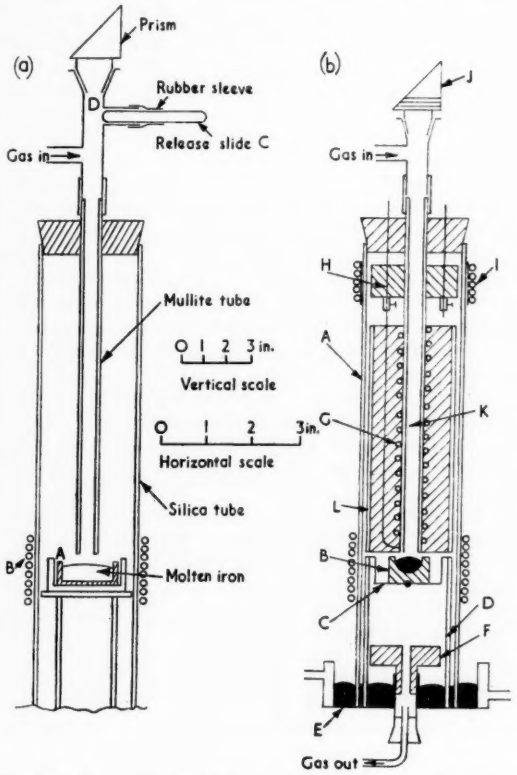


Fig. 1—(*a*) Apparatus for preparation of iron–phosphorus master alloys; (*b*) reaction system for equilibrium measurements

froze quickly, and care was necessary to apply suction at a suitable rate. As a safety measure, a piece of thick copper wire was inserted in the upper end of the silica tube to chill and freeze metal that had been accidentally sucked up too far. The tube, carrying the frozen rod of master alloy, was lifted out of the apparatus and cooled in water; the procedure was repeated until the crucible was empty. By cracking away the silica tube, the rods of master alloy were obtained. They were dried to prevent rusting.

Transverse sections of the chilled master-alloy rods showed very satisfactory constancy in phosphorus content (*e.g.*, in one case, analyses of successive rods gave 0·93%, 0·94%, 0·95%, 0·96%, 0·95%, and 0·94% P); because of the radial freezing, any segregation would have occurred between the circumference and the centre of the rod.

Phosphorus master alloys were also prepared by the alternative method of heating iron and ignited ferric phosphate in hydrogen. This method was less satisfactory at the higher phosphorus contents, because of the considerable bulk of the necessary quantities of phosphate.

Determination of Phosphorus

The equilibrium measurements depended on analytical determination of phosphorus transfer between the liquid iron and lime–phosphate phases, and it was necessary to devise reliable methods of analysis for iron containing 0·005–5% of phosphorus, and for lime containing small quantities of phosphate. In the methods eventually used, the phosphorus was determined gravimetrically and weighed as phosphomolybdic anhydride, $P_2O_5,24MoO_3$.

Determination in Iron—For determination of phosphorus in the iron phase, 2 g. of the iron were dissolved in 30 ml. of dilute (1 : 1) nitric acid, and the solution was boiled. 10 ml. of 2% potassium permanganate solution were added to ensure complete oxidation of the phosphorus; after boiling for 2 min., saturated sulphur dioxide solution was added dropwise until precipitated manganese oxides dissolved. The solution was again boiled for 3 min. to expel sulphur dioxide, and then allowed to cool. The ensuing precipitation was carried out on the whole of the solution or on a suitable aliquot portion, according to the expected phosphorus content.

For the ammonium phosphomolybdate precipitation, 10 ml. of concentrated ('0·880') ammonia solution were added; the hydrated ferric oxide precipitate was at once dissolved by addition of concentrated nitric acid, 2–3 ml. of which were added in excess. Distilled water was added to bring the volume of liquid to 60 ml., and the temperature was raised to 60° C. 35 ml. of ammonium molybdate solution were then added slowly, with continual stirring. The beaker and contents were kept at 60° C. for ½ hr., and then left to cool overnight so as to complete precipitation of the ammonium phosphomolybdate. The precipitate was filtered on a porous-based glass filter crucible (porosity 4), and washed with a solution containing 0·8% of ammonium nitrate and 0·5% of nitric acid. The crucible and precipitate were placed in a small electric muffle furnace and heated to 425° ± 10° C., which temperature was maintained for 1½ hr. The crucible was cooled, weighed, and reheated until constant in weight. The bluish-black residue of phosphomolybdic anhydride was not appreciably hygroscopic.

The ammonium molybdate solution was prepared by suspending 100 g. of molybdic oxide in 240 ml. of water, and dissolving it by addition of 170 ml. of concentrated ammonia solution. The solution was poured into 1250 ml. of nitric acid (density 1·20), containing a little phosphate. The reagent was allowed to stand for at least 24 hr. before use, and portions taken from stock were filtered.

After each determination, phosphomolybdic anhydride was readily removed from the crucible by treatment with equal volumes of concentrated ammonia and '20-volume' hydrogen peroxide solutions.

The method described was unreliable when used on samples containing more than 2 g. of iron, because of incomplete precipitation. With the very low phosphorus contents (less than 0·01%), a 4-g. sample was used and the quantities of reagents were doubled.

Tests of the method were made by analysing a steel issued by the Bureau of Analysed Samples, stated—on the basis of several independent analyses—to contain 0·083 ± 0·002% of phosphorus; duplicate analyses gave 0·082 and 0·083% of phosphorus. Excellent concordance was always obtained between aliquots or duplicate analyses of master alloys or equilibrium samples (*e.g.*, 0·043%, 0·043%; 0·061%, 0·062%; 0·177%, 0·177%; 0·90%, 0·90%; 1·46%, 1·48%; 2·04%, 2·02%).

Determination in Lime—Samples of lime, containing phosphate, were usually about 4 g. in weight, with a phosphorus content of about 0·005%. The lime was slaked with water and dissolved in nitric acid, and the solution diluted to 60 ml. The ammonium molybdate precipitation was then carried out, and the determination was completed according to the details already given.

Apparatus for Equilibrium Measurements

Preparation of Controlled Atmospheres of Hydrogen and Water Vapour—The apparatus used to prepare

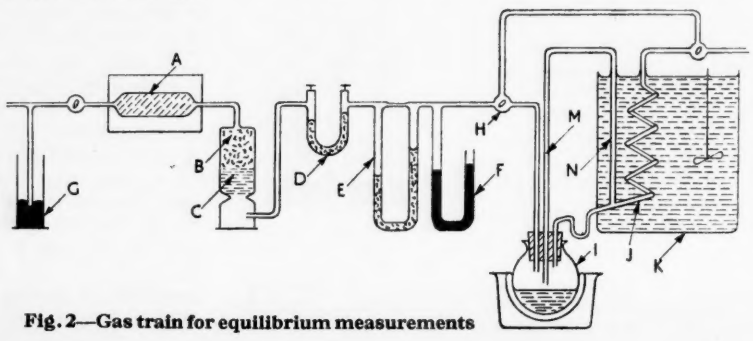


Fig. 2—Gas train for equilibrium measurements

controlled atmospheres is shown in Fig. 2. 'Oxygen-free' hydrogen from a commercial cylinder was passed over palladinized asbestos *A* in a 'Pyrex' tube heated to 350° C. by a small electric furnace, to convert traces of oxygen into water vapour. The gas then passed through 'Sofnolite' *B*, anhydrous calcium chloride *C*, and 'Anhydrone' *D*, to remove acidic gases and moisture. The purified hydrogen, after passing through the flowmeter *E*, was saturated with water vapour, at an accurately known saturation temperature, in the thermostatically controlled water-bath *K*. Distilled water was boiled gently in the flask *I*, into which the hydrogen passed; gas containing a substantial excess of water vapour flowed up the lagged tube *M*, and eventually into the long glass spiral *J*, in which saturation equilibrium was reached at the temperature of the water-bath. Most of the excess water condensed in the tube *N* and in the first of the ten turns of the glass spiral.

The water-bath was controlled to $\pm 0{\cdot}05°$ C., at readily predetermined temperatures, by a standard toluene–mercury regulator operating in conjunction with a 'Sunvic' vacuum switch and electric heater; thorough stirring was essential. Saturation temperatures were measured by a mercury thermometer, divided to 0·2° C., which was calibrated against a similar thermometer standardized by the National Physical Laboratory.

A mercury 'blow-off' *G* was provided to guard against development of high pressures in the gas train; and the hydrogen flow-rate and pressure, respectively, were measured by a flowmeter *E*, of conventional design, and a mercury manometer *F*. A two-way tap *H* allowed dry hydrogen to be by-passed through to the equilibrium-measurement apparatus, when necessary. As the saturation temperature was always above room temperature, all connecting tubing through which the wet gas passed was lagged with asbestos paper, and was kept warm by a suitable electric heater winding of 'Nichrome' wire. Taps in this section of the apparatus were lubricated with a silicone grease, claimed to be serviceable at 200° C.

Reaction System for Equilibrium Measurements—All iron melts used for equilibrium measurements were heated by induction. This simplified refractory problems considerably, and made the whole apparatus simple and readily adaptable. The high-frequency generator used was a standard valve oscillator, operating at 800 kilocycles/sec. and giving a maximum output of 5 kVA. The generator itself contained controls for smooth adjustment of power output. The induction coil used to heat the specimen comprised 20 close-wound turns of copper tubing, through which water was passed for cooling; the turns were insulated by a casing of fibreglass tubing, varnished with a special silicone insulating resin.

The main apparatus is illustrated in Fig. 1*b*. The outer tube *A* was a sand-finished silica tube, 6 cm. dia. × 60 cm. long, with a wall thickness of about 5 mm. The crucible *B* rested on 1-mm. molybdenum cross-wires *C*, which facilitated its accurate location in the apparatus; the cross-wires were supported on a suitably fashioned piece of mullite tubing *D*, standing in a water-cooled mercury well *E*, and centred by a brass 'mushroom' *F* resting in the fixed exit tube.

The danger of thermal diffusion[5] made it necessary to preheat the gas impinging on the iron melt. The controlled atmosphere was therefore led in through a sintered alumina or mullite tube *K* ($\frac{3}{8}$-in. dia.), carrying a molybdenum preheater winding *G* over the lower 9 in. of its length. The winding was of 0·35-mm. wire, wound at ten turns to the inch over the bottom inch, and eight turns to the inch for the remainder of the winding. The bottom of the preheater projected into the high-frequency field of the induction heater, and it was therefore necessary to terminate the winding without a continuous anchor ring of wire or strip round the tube. A mullite tube *L*, which was a close fit inside the outer silica tube, was attached concentrically to *K* by means of alundum cement, and the annular space between the two tubes was filled with fused alumina granules. The preheater winding was supplied from a transformer with a continuously variable output voltage; currents required to maintain the necessary preheater temperatures were determined by preliminary experiments in which an optical pyrometer was sighted on the inner wall of the preheater tube. The preheater consumed about 1·5 kW.

The top of the silica outer tube was closed by a large rubber bung, protected from heat radiation by a suitably shaped cylindrical block of refractory brick *H*, and cooled by water-cooling coils *I*. A glass prolongation of the preheater tube *K* carried a gas inlet tube and the 90° prism *J*, through which the interior of the apparatus could be observed; as this section of the apparatus carried wet hydrogen, lagging and heating by the usual 'Nichrome' spiral were necessary. The prism was cemented to the glass tube by means of 'Durofix,' an adhesive which resists the action of heat and water vapour. Occasionally it was necessary to lower the cooling coils *I*, to prevent condensation of water in the upper, cooled part of the apparatus.

Temperature Measurements

All temperature measurements were made with a disappearing-filament pyrometer designed by the National Physical Laboratory, where it was calibrated in terms of the current through the filament of the standard lamp. During measurements, the current, which was supplied from a nickel–iron accumulator, was measured by a standard resistance and potentiometer, or by an accurate ammeter with a suitably long scale; both types of measuring equipment were periodically checked against standards.

The surface of the iron melt was viewed by the pyrometer through the prism *J* (Fig. 1*b*), which allowed the pyrometer to be mounted conveniently. The determination of the true temperature of the iron by application to the apparent temperature of a simple emissivity correction (as determined by Dastur and Gokcen[7]) was prevented by the reflection of the hot preheater wall in the surface of the melt. Instead, true temperatures were determined from the relationship $1/T - 1/T' = K$, where T is the true temperature, in ° K., T' is the apparent temperature, in ° K., and K is a constant. The value of K was determined from the apparent melting point of iron, at which T

was 1808° C. This relationship was assumed to hold under the conditions of the experiment; *i.e.*, with a hot preheater above the melt. It also assumes that the emissivity of the iron did not vary when up to 1% of phosphorus was added. Confirmation of this assumption was obtained when the course of melting of a 1% phosphorus alloy was observed through the optical pyrometer. The range was that indicated by the iron–phosphorus phase diagram,[8] without any correction being applied for variation of emissivity.

Fabrication of Crucibles

Runs were carried out in crucibles of two types, in which the inner surfaces in contact with the metal consisted, in one case, of pure lime, and, in the other, of lime mixed with tetracalcium phosphate.

Pure lime crucibles were prepared by several different methods. Blocks of lime made by firing white Sicilian marble were too friable to drill, and techniques involving the pressing of a stiff paste in a suitable mould were adopted. Moderate success was achieved by pressing ball-milled lime (prepared by firing calcite), moistened with alcohol; the pressed crucible was removed from the mould while still damp, and fired at 1600° C. in hydrogen by induction heating inside a molybdenum crucible. More consistent results, with less labour, were obtained by pressing a stiff paste of precipitated calcium carbonate ('AnalaR') and water, and heating the damp pressing (which was sufficiently robust to handle) to 1000° C. over a period of three hours. Crucibles prepared by this method, which were porous but not unduly soft, were stored in a desiccator; although some were fired at 1450° C. before use, such firing proved not to be essential, and crucibles were successfully used in most equilibrium measurements without any special pretreatment. Lime crucibles made by such means withstood heating of iron to its melting point, from ambient temperatures, in one minute; sintering and crazing of the inner surface occurred, but without fracture.

Crucibles containing tetracalcium phosphate (referred to later as 'phosphate crucibles') were made by adding a lining to pressings of moist calcium carbonate; the inner (male) portion of the mould was removed, and about 0·3 g. of a 2 : 1 mixture of calcium carbonate and tetracalcium phosphate, moistened with water, was dropped into the crucible cavity. The inner part of the mould was then replaced and the crucible was finished in the usual way. Tests with a coloured paste showed this procedure to give a uniform lining of the crucible.

A cross was cut in the base of each crucible to register with the molybdenum cross-wires (*C* in Fig. 1*b*) in the reaction system.

Procedure in Equilibrium Measurements

The procedure adopted to carry out an equilibrium measurement is summarized as follows:

(1) The water-bath of the hydrogen saturator was adjusted to the temperature necessary to give the desired water-vapour pressure.

(2) Suitable quantities of pure iron and of phosphorus master alloy were weighed, and placed in a lime or phosphate crucible; sometimes it was convenient to pre-melt the iron (in hydrogen) in a lime crucible before adding the phosphorus alloy.

(3) The whole reaction system was assembled, and ancillary supplies (such as cooling water, connecting tube, palladinized asbestos heaters, etc.) were switched on. The reaction tube was then flushed with a rapid stream of dry hydrogen.

(4) The hydrogen flow-rate was reduced to 200 ml./min., and the preheater was switched on and heated to the required temperature; as this was approached, sufficient H.F. current was supplied to heat the iron to about 800° C. This allowed adjustment of the position and focusing of the optical pyrometer.

(5) The H.F. supply was turned full on, to melt the iron quickly; slow melting tended to proceed from the bottom of the ingot and to leave an intractable scaffold of solid metal at the top. Freezing and remelting of the iron at this stage allowed a check of the optical pyrometer. The H.F. input was finally adjusted to bring the metal to the desired working temperature. With phosphate crucibles, the water-vapour saturation system was connected as soon as heating of the iron from 800° C. was begun, to prevent extensive reduction of phosphate and transfer of phosphorus to the iron; with lime crucibles, water vapour was admitted later, when the working temperature was being reached.

(6) Reaction was allowed to proceed for four hours, during which time frequent checks of the working temperature were made. Towards the end of the period, the barometer was read, and the total gas pressure in the reaction system was found by adding the observed pressure excess at manometer *F* (Fig. 2).

(7) The H.F. supply and ancillary supplies were cut off, and the reaction system was cooled with dry hydrogen passing through the tube. When cool, the apparatus was dismantled, and the crucible and ingot were removed for analysis.

RESULTS

Equilibrium Measurements in Phosphate Crucibles

Equilibrium measurements were carried out at each of the three temperatures 1540°, 1560°, and 1580° C. Attempts to make measurements at 1600° C. indicated that the lime–phosphate eutectic temperature had been exceeded. At the three different temperatures, runs were divided into groups, in each of which the water vapour to hydrogen ratio in the controlled atmosphere was kept constant at a selected value. A group comprised a number of runs (usually six or seven), with different initial phosphorus contents in the metal phase. Each run was carried out by the procedure already described and, after thorough mechanical cleaning and etching with nitric acid to remove crucible material, the iron ingot was cut vertically into two equal halves, and one half analysed for phosphorus; the second half was retained for a duplicate analysis or for examination by other means.

A typical group of measurements showed the expected phosphorus losses to the crucible from melts initially high in phosphorus, and gains from the crucible in low-phosphorus melts. The gains (positive)

or losses (negative) were plotted as ordinates against the initial phosphorus content of the melt; the plot could be satisfactorily represented by two straight lines, for gains and losses respectively, both of which cut the phosphorus-content axis at the equilibrium value. At low phosphorus contents, the gain and loss plots coalesced to a single line. By this method of extrapolation, the need for a close approach to the actual equilibrium phosphorus content, by successive trials, was eliminated, and the reality of approach to equilibrium conditions from either side was repeatedly proved.

Figure 3 records the results obtained at 1540° C., the equilibrium phosphorus contents being plotted against the pressure ratio of water vapour to hydrogen; an oxygen-activity scale (*see* below) is also included. Each numbered point represents equilibrium conditions derived in a corresponding group of measurements; Fig. 3 actually contains the results of 65 runs.

The reaction studied directly was

$$2[P] + 5H_2O\ (gas) + 4CaO\ (solid) \rightleftharpoons Ca_4P_2O_9\ (solid) + 5H_2\ (gas) \ldots\ldots (2),$$

and the equilibrium constant of this reaction is given by

$$(p_{H_2}/p_{H_2O})^5(1/a_{[P]})^2 = K_2 \ldots\ldots\ldots\ldots\ldots\ldots (2a)$$

or

$$\log_{10}(p_{H_2O}/p_{H_2}) = -\tfrac{2}{5}\log_{10}a_{[P]} - \tfrac{1}{5}\log_{10}K_2 \ldots\ldots (2b)$$

Clearly a plot of $\log_{10}(p_{H_2O}/p_{2H})$ against $\log_{10}a_{[P]}$ (or assuming the solution of phosphorus to obey Henry's Law, $\log_{10}(\%P)$) should be linear and possess a slope of $-\frac{2}{5}$ (*i.e.*, $-0{\cdot}40$). Such plots for the data obtained at 1540° C., 1560° C. (34 runs), and 1580° C. (16 runs) are shown in Figs. 4*a*, *b* and *c*. The plots have the ideal slope of $-0{\cdot}40$ at phosphorus contents greater than 0·8%, 0·1%, and 0·03%, respectively; at lower phosphorus contents the slopes have abnormally high negative values. Reasons for the abnormality will be considered later.

The linearity and ideal slope of each of the plots shown in Figs. 4*a*, *b* and *c* for phosphorus contents in the neighbourhood of 1% suggest that phosphorus may be considered to behave according to Henry's Law in liquid-iron solution at this concentration. On this basis, $a_{[P]}$ may be set equal to unity at a concentration of 1%, and values of K_2 may be computed from the corresponding values of p_{H_2O}/p_{H_2} deduced from Figs. 4*a*, *b* and *c*. Values of the standard free-energy change for reaction (2) ($\Delta G^\circ_2 = -RT\log_e K_2$) may then be calculated; the results are shown in Table I. The straight line

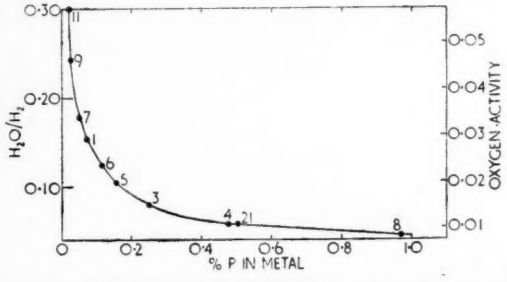


Fig. 3—Plot of equilibrium measurements in phosphate crucibles at 1540° C.

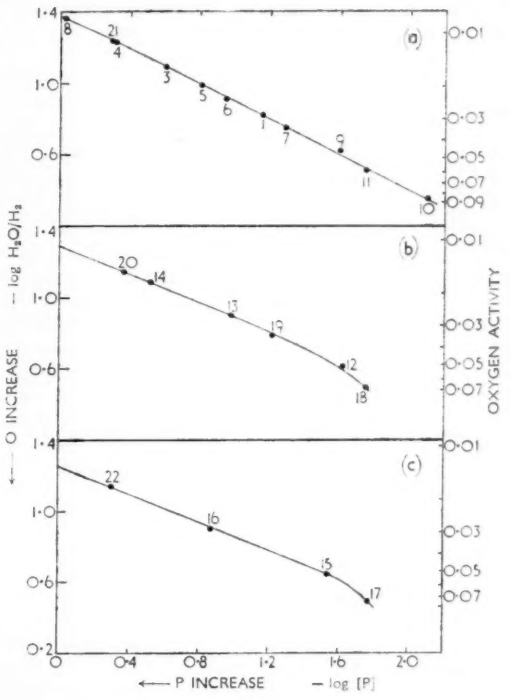


Fig. 4—Logarithmic plot of equilibrium measurements in phosphate crucibles at (*a*) 1540° C., (*b*) 1560° C., and (*c*) 1580° C.

considered to represent a plot of the three ΔG°_2 values against T (some added weight being given to the values at the higher temperatures) has the equation:

$$\Delta G^\circ_2 = (-187{\cdot}9 + 0{\cdot}0729T)\text{kg.cal} \ldots\ldots (2c)$$

Values of ΔG°_2 calculated from equation (2*c*) are compared with the experimental values in Table I.

The oxygen activity in liquid iron in contact with hydrogen and water vapour is governed by the equation:

$$H_2O\ (gas) \rightleftharpoons [O] + H_2\ (gas) \ldots\ldots (3)$$

$$a_{[O]}(p_{H_2}/p_{H_2O}) = K_3 \ldots\ldots (3a)$$

Values of the standard free-energy change of this reaction have been given by Dastur and Chipman[5, 6]:

$$\Delta G^\circ_3 = (32{\cdot}25 - 0{\cdot}01457T)\text{kg.cal} \ldots\ldots (3b)$$

Table I

STANDARD FREE-ENERGY CHANGES (IN KG.CAL.) FOR REACTIONS (1) AND (2)

Temperature		ΔG°_2		ΔG°_1
° C.	° K.	(Experimental)	(Calculated from Equation 2*c*)	(Calculated from Equation 1*c*)
1540	1813	−56·8	−55·7	−85·4
1560	1833	−54·1	−54·2	−82·6
1580	1853	−53·0	−52·8	−79·7

Equations (2) and (3) can be combined to give equation (1) (*see* p. 404). Also:

$$\frac{1}{a^2_{[P]}.a^5_{[O]}} = K_1 = K_2/K_3{}^5 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1b)$$

and

$$\Delta G^\circ_1 = \Delta G^\circ_2 - 5\Delta G^\circ_3 = (-349{\cdot}1 + 0{\cdot}1454T) \text{ kg.cal.} \quad \ldots\ldots (1c)$$

Values of ΔG°_1, deduced from this equation, are shown in Table I. ΔG°_1 values are of more general use, but ΔG°_2 does not incorporate experimental values of ΔG°_3, and must be used as a basis for new calculations if ΔG°_3 data are revised by later measurements.

It must be emphasized that, whereas the free-energy changes of the reactions studied are correct to within the limits set out in the Discussion, this is true only at the temperatures actually studied. Because the measurements could be made only over a small temperature range, the quoted temperature dependence of the free energies is subject to some uncertainty, and this must be borne in mind if the free-energy values are extrapolated far from the temperature range studied.

Equilibrium Measurements in Lime Crucibles

Equilibrium could be reached in lime crucibles only by transfer of phosphorus from the metal phase to the crucible. The technique of measurement was therefore to carry out a series of runs (at a fixed temperature and p_{H_2O}/p_{H_2} ratio) with increasing amounts of phosphorus in the melt, and to locate the phosphorus content at which appreciable transfer from metal to crucible began.

Determination of phosphorus transfer was effected by analysis of the crucible rather than of the residual iron ingot: small phosphorus gains in lime were determined more accurately than differences between relatively large initial and final phosphorus contents in the iron. After each run, the crucible and contents were placed in a covered beaker, and the lime was slaked by cautious addition of water; after dilution and gentle boiling, the iron bead could be removed almost free from lime. The last traces of lime on the bead were removed by further boiling with a little water, and finally by rinsing with 1% nitric acid, which attacked the bead itself to a negligible extent. The lime suspensions and extracts were combined, agitated with a magnet to remove particles of metallic iron, and analysed for phosphorus by the method described earlier. A check determination of phosphorus in the bead was made, to provide confirmation of any phosphorus transfer.

The necessary provision of an interface of phosphate-containing lime against the liquid iron resulted in some absorption of phosphorus into the crucible, even at low initial phosphorus contents in the melt. Nevertheless, as the initial phosphorus content was raised by small increments in successive runs, a value was eventually reached at which the gain by the crucible showed a sudden jump; the final phosphorus content of the melt at this point was taken as the equilibrium value. The reality of the jump was shown by plotting phosphorus transfer to the crucible (expressed as the percentage of phosphorus on the initial weight of the bead) against initial phosphorus content; this necessitated a few check runs with initial phosphorus contents higher than the equilibrium value.

The equilibrium points obtained at 1540° C. are plotted (as equilibrium phosphorus content against p_{H_2O}/p_{H_2}) in Fig. 5*a*; a corresponding logarithmic plot is shown in Fig. 5*b*, with the line obtained by measurements on phosphate crucibles shown dotted for comparison. Measurements at other temperatures were not made.

The significant difference between the two lines in Fig. 5*b* is noteworthy. As the lines are parallel for most of their length, they both appear to refer to the same phosphorus–oxygen equilibrium *in the melt*; the vertical displacement implies that the solid phases operating are different in the two cases. The difference was eventually traced to the presence of silicon in the iron. The iron and master alloy used contained about 0·008% of silicon. Thermodynamic considerations indicate that almost all this silicon would be transferred to the lime, under the conditions of the experiments, as dicalcium silicate. Because of this, if iron is melted in a lime crucible in a water–hydrogen gas mixture for some time, it is effectively 'desiliconized.' When such previously 'desiliconized' iron was used in the runs, the iron did not lose phosphorus to the lime, as it did before treatment; phosphorus losses became significant only when the phosphorus content of the melt exceeded that corresponding with the tetraphosphate equilibrium at the same gas ratio. When silicon was deliberately added to 'desiliconized' melts, they again behaved in the normal manner.

This aspect of the work is presented diagrammatically in Fig. 6, which shows phosphorus transfer to the crucible with varying amounts of silicon in the iron, all at $p_{H_2O}/p_{H_2} = 0{\cdot}103$. The point on the top line shows the result of an ordinary run, using a lime crucible. The initial phosphorus content was more than the equilibrium value, and the loss to the crucible was of the usual order. The second line shows

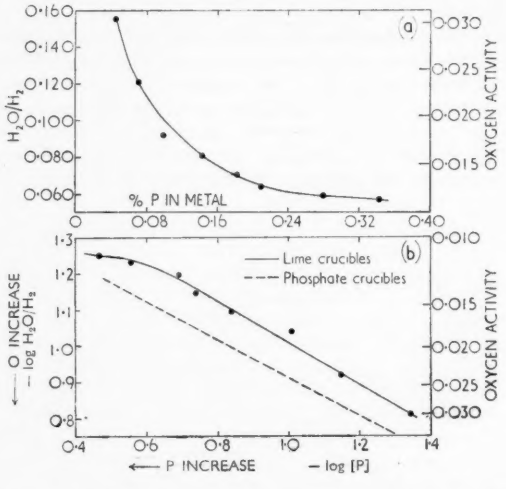


Fig. 5—Plot of equilibrium measurements in lime crucibles at 1540° C.: (*a*) linear plot, and (*b*) logarithmic plot

results of runs using 'desiliconized' iron. Although the initial phosphorus contents were considerably greater than the equilibrium value, no significant amount of phosphorus was lost until the phosphorus concentration exceeded the phosphate equilibrium value, when the loss was 0·014%, which was larger than normal losses with lime crucibles. The third line shows the effect of adding silicon to previously 'desiliconized' iron; the melt lost phosphorus in the normal manner. At the end of the runs involving the addition of silicon to the iron, the beads were analysed for silicon. Although 0·05% of silicon was added, the final silicon content was less than 0·01%. This confirms the 'desiliconization' of the iron by the lime crucibles.

The solid phosphate phase formed in the presence of silicon was eventually concluded, by consideration of the $CaO–SiO_2–P_2O_5$ phase diagram, to be the calcium silicophosphate *nagelschmidtite*, $9CaO,P_2O_5,3SiO_2$. The presence of a large excess of lime defeated attempts to identify this product positively by X-ray powder photography. Consideration of relevant free-energy data indicates that in the runs in lime crucibles, silicon introduced with the iron is first oxidized to Ca_2SiO_4, which reacts with phosphorus and oxygen from the melt and with more lime to give nagelschmidtite; the operative equilibrium is:

$$2[P] + 5[O] + 3CaO\ (solid) + 3Ca_2SiO_4\ (solid) \rightleftharpoons 9CaO,P_2O_5,3SiO_2.$$

The standard free-energy change for this reaction, at 1540° C., is derivable from the line in Fig. 5*b* as − 88 kg.cal.

Nagelschmidtite did not participate in the equilibria observed in phosphate crucibles, because sufficient phosphate was present to convert all the available silicon to silicophosphate and still leave an excess for direct reaction with liquid iron.

Oxygen Contents of Iron Melts Containing Phosphorus

Four 70-g. samples of iron, containing phosphorus, were held at 1540° C. in controlled atmospheres of hydrogen and water vapour, for one hour, and then quenched. Alumina crucibles were used in these experiments. The ingots were analysed for total oxygen content by the vacuum-fusion method, at the National Physical Laboratory. Table II shows the results, togther with oxygen contents calculated from the p_{H_2O}/p_{H_2} ratios and the data of Dastur and Chipman[6] for pure iron.

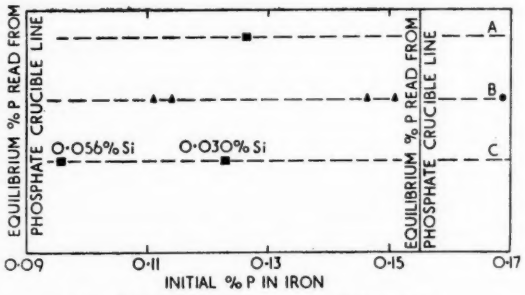


Fig. 6—Effect of silicon on equilibria in lime crucibles. All at $H_2O/H_2 = 0·103$

Table II

OXYGEN CONTENTS OF IRON INGOTS CONTAINING PHOSPHORUS

Sample	% P	% O by Vacuum Fusion	Calculated % O
A	0·101	0·015, 0·014	0·024
B	0·100	0·010, 0·011	0·014
C	0·300	0·013, 0·017	0·024
D	0·300	0·010, 0·012	0·014

The difference is erratic and does not appear to be related to the phosphorus content. Indeed, if—as explained later—oxygen lowers the activity coefficient of phosphorus, the effect of phosphorus should be to increase rather than to diminish the oxygen contents. The explanation of the low values appears to lie in the fact that the ingots obtained from the melt were very porous, owing to evolution of gases on solidification. The melts were inevitably saturated with hydrogen, so that as much as 0·001 wt.-% (1·6 relative volumes at S.T.P.) should be evolved on freezing. This might carry away with it as much as 0·004 wt.-% of oxygen as steam. In addition, small amounts of carbon were present (~ 0·01%), and these could also carry away significant quantities of oxygen on freezing, owing to formation of carbon monoxide.[4]

Calcium Phosphate Inclusions in Ingots used for Equilibrium Measurements

The possibility of errors in analysed phosphorus contents in iron ingots, arising from calcium phosphate inclusions, made suitable tests desirable. Two typical ingots were therefore analysed for calcium by the Bragg Laboratory, Sheffield; none was found spectrographically, but chemical analysis by an unspecified method showed a 'trace.' Appreciable errors from inclusions are therefore unlikely.

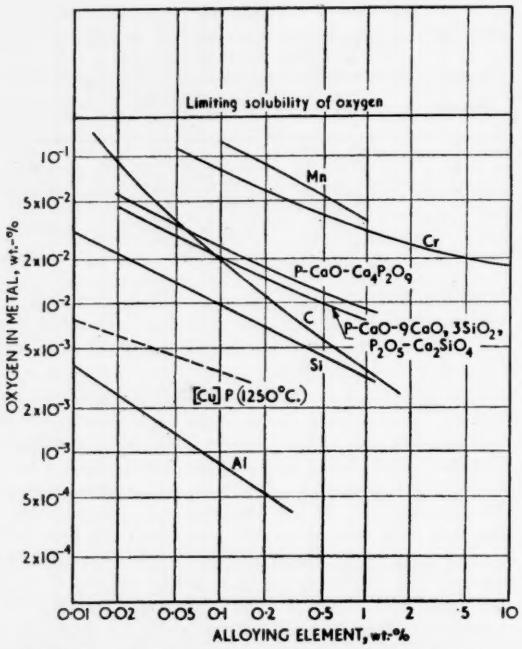
DISCUSSION

Accuracy of Free-Energy Values

A review of possible sources of error indicates that temperatures reported in this paper should be correct to ± 5° C., p_{H_2O}/p_{H_2} ratios to ± 2%, and equilibrium phosphorus contents (above 0·03%) to ± 3%. These probable errors lead to an estimated error of ± 0·5 kg.cal. in the standard free-energy values quoted in Table I.

The Influence of Oxygen on the Activity Coefficient of Phosphorus

The anomalously large negative slopes of the plots in Figs. 4*a*, *b* and *c*, at low phosphorus concentrations, are considered to be due to a lowering of the activity coefficient of phosphorus by the dissolved oxygen. On this assumption, it can be calculated that, at 1540° C., the phosphorus activity coefficient is unity at 0·009% oxygen *activity* (0·80% P *concentration*), and that it falls to 0·36 at 0·076% oxygen (0·01% P). At 1560°



Full lines: Deoxidation by phosphorus and other elements at 1540° C. in liquid iron
Broken line: Deoxidation by phosphorus in liquid copper at 1250° C.
Equilibrium non-metallic phases (from top to bottom): liquid MnO–FeO; solid $FeO.Cr_2O_3$ and Cr_2O_3; solid CaO, $Ca_4P_2O_9$; solid CaO, Ca_2SiO_4, $9CaO.P_2O_5.3SiO_2$; gaseous CO, CO_2; solid SiO_2; liquid Cu_2O–P_2O_5; solid Al_2O_3.

Fig. 7—Comparative deoxidizing powers of phosphorus and other elements

C., the influence of oxygen is negligible up to 0·03% oxygen (0·075% P), and at 1580° C. it is negligible up to 0·057% oxygen (0·024% P).

Although interaction between phosphorus and oxygen is quite possible, it is somewhat surprising that it decreases so markedly with temperature. For this reason, a more detailed study of the influence of phosphorus on the activity coefficient of oxygen is now being undertaken.

Phosphorus as a Deoxidizer

It is not possible to review these new results in relation to the thermodynamics either of phosphorus in liquid iron or of the other calcium phosphates, except on the basis of the approximate calculations mentioned earlier.[9] Since further experiments designed to elucidate the thermodynamics of the calcium phosphates have now been nearly completed by one of us (J.B.B.), such considerations will be left to a later paper. It is, however, of some interest to consider the relationship which has clearly been established between phosphorus and oxygen in liquid iron. In the presence of the solid phases used in this investigation, the phosphorus and oxygen activities are connected through the relationship $a^2_{[P]}.a^5_{[O]} = K$, so that phosphorus is, in a sense, a deoxidizer for liquid iron. In steelmaking practice, phosphorus is controlled by means of a complex liquid slag, in which the phosphorus is held in phosphate or silicophosphate groups or ions. It follows that for these conditions also, a similar $a^2_{[P]}.a^5_{[O]}$ relationship must apply so far as the metal side of the equilibrium is concerned.

It is also of interest to compare the deoxidizing power of phosphorus with that of other elements on a typical deoxidation diagram, as shown in Fig. 7. The phosphorus curves differ slightly from the others, in that the relevant oxygen values are percentage *activities* instead of *concentrations by weight* (the influence of phosphorus on the activity coefficient of oxygen is not known).

As phosphorus is used as a deoxidizer for copper, its behaviour in this connection is also shown in Fig. 7. The broken line, which is taken from Baker,[1] represents the deoxidation at 1250° C., the phase in equilibrium with the metal being a liquid copper–phosphate slag. Although the P_2O_5 activity in the copper–phosphate slag is much higher than in the lime systems used here, deoxidation is much more efficacious in the case of copper. This is because copper holds dissolved oxygen at a far higher chemical potential than does iron.

Acknowledgments

The generous support of the British Iron and Steel Research Association throughout the course of the work reported in this paper is gratefully recognized. This support included the award of a Bursary to one of the authors (J.B.B.) and provision of numerous items of equipment. The final measurements were made in the Battersea Laboratories of the Association. The interest of Sir Charles Goodeve and Dr. J. Pearson has been warmly appreciated. Use has been made of X-ray equipment provided by the Royal Society, and of a muffle furnace contributed by the Central Research Funds of the University of London. Mr. L. S. Theobald kindly advised the authors on methods of determining phosphorus in iron.

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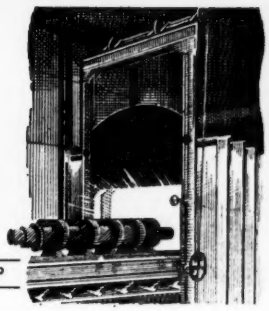
IRON AND STEELWORKS ENGINEERING

THE IRON AND STEEL ENGINEERS GROUP



DESCRIPTION OF NEW PLANT

The New Heavy Forge at Hadfields Ltd.

MESSRS. Hadfields Ltd. have recently erected and equipped a completely new forge unit to meet the present and future requirements for larger forgings in special highly alloyed steels. It has two air-hydraulic forging presses of very modern design, one of 2700 tons and the other of 1500 tons capacity, and the necessary reheating and heat-treatment furnaces.

This unit has been designed to handle ingots up to 45 tons in weight, and to produce forgings up to 40 in. dia. or up to 40 ft. long, rings up to 12 ft. dia., and sleeves up to 6 ft. long.

The general layout and the choice and design of individual units have been determined with the object of effectively and economically dealing with both present and future requirements, in the correct production sequence.

The building, which is of the usual steel-framed mill construction, occupies an area of 122,000 sq. ft. and consists of four bays. The heat-treatment bay and furnace and forge bays each have a crane span of 80 ft. 0 in., with a height of 52 ft. 0 in. from floor to crane rail level, and a total length of 386 ft.; and the stock bay is of the same length, but has a crane span of 51 ft. 9 in. and a height from floor level to crane rail of 39 ft. 6 in.

FORGING PLANT

The two forging presses are operated by a common pressure water plant, and their location is shown in Fig. 1, which gives a layout plan of the forge.

One of the main features of the press plant is its very high working speed and ease of operation over a wide range of forging work. To make this possible, and also to allow for the greatest flexibility, it was decided to install an air-hydraulic accumulator station, in preference to a direct pump drive installation.

Results so far have shown that penetration speeds of 6 in./sec. or more can be achieved on both presses at full power, and for planishing or finishing operations well over 100 strokes per min. have been maintained. These high operational speeds are of particular advantage from both economic and metallurgical aspects in the forging of many of the special highly alloyed steels, whose inherent properties may impart a very restricted hot working temperature range.

Interesting characteristics of the presses are the following:

2700-ton Press

This is a three-cylinder vertical-type press, and is hydraulically operated. Each cylinder is capable of exerting 900 tons pressure, and the controls are so arranged that either the centre cylinder, the two outer cylinders, or all three cylinders can be employed. This enables the operator to select at will a pressure stage of 900, 1800, or 2700 tons.

The two outer rams are attached to the moving crosshead, and their cylinders are fitted to the top entablature, by retaining rings, in the orthodox manner; *i.e.*, the rams move and the cylinders are fixed. The centre ram, however, is reversed: the ram is fixed to the top entablature by means of a small crosshead and secured by bolts, and the centre cylinder is rooted into the moving crosshead. A brass bush, fixed on the outside of the top end of the centre cylinder, slides inside a cast-iron sleeve shrunk into the top entablature; thus, guiding throughout the stroke is maintained. The press has a stroke of 7 ft. 6 in. and a maximum daylight of 14 ft. 0 in. At the bottom of the moving crosshead, four phosphor-bronze split bushes are fitted, and act as column guides; at the top, four oil-retaining felt washers engage with the columns.

1500-ton Press

The 1500-ton press resembles in many respects the larger press, the essential differences being that it is a single-cylinder vertical type of 1500 tons power,

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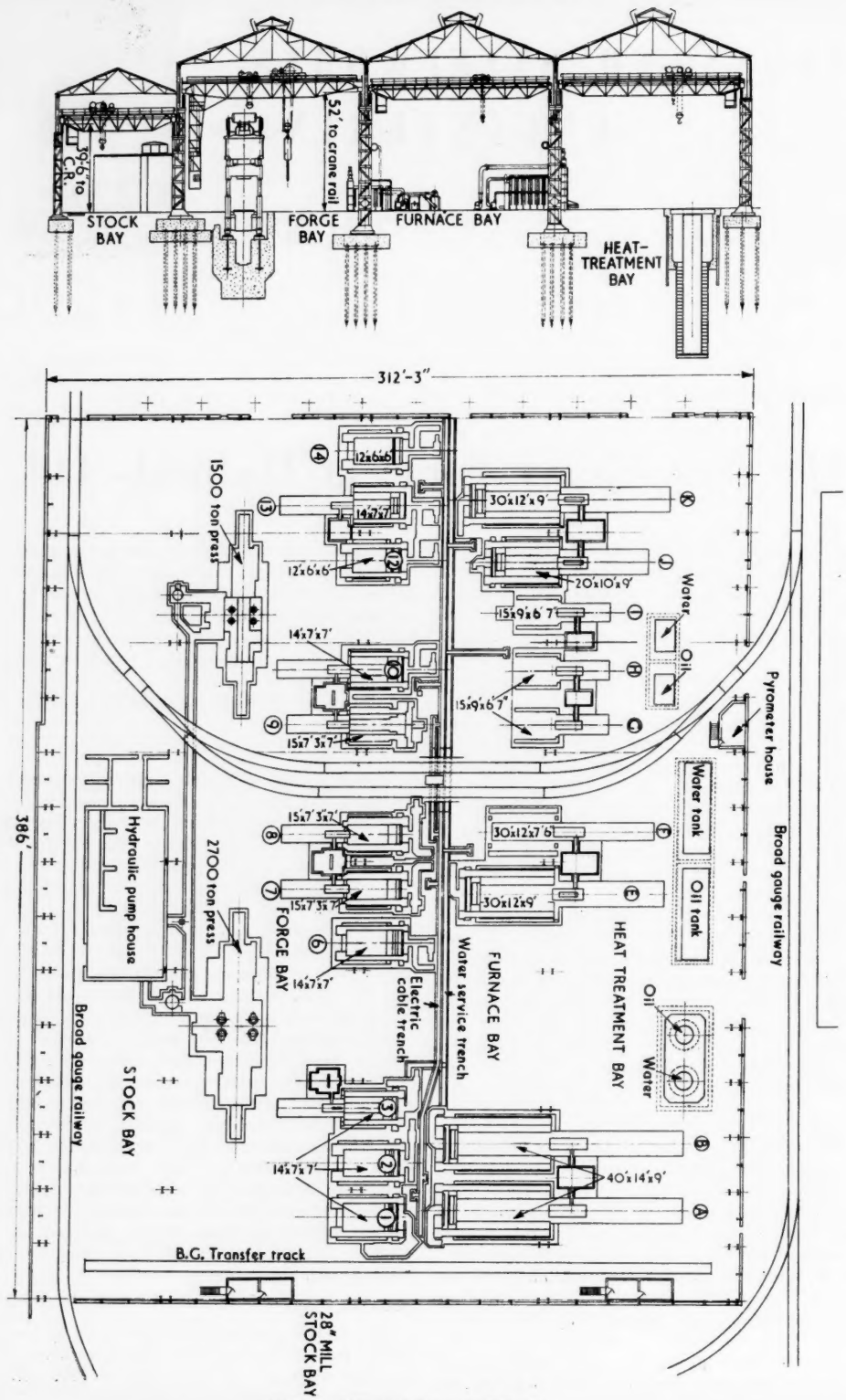

Fig. 1—General layout of forge

and the crosshead retaining the centre ram is embodied in the top entablature casting ; and that it has a stroke of 6 ft. 0 in., and the maximum daylight is approx. 11 ft. 0 in.

Characteristics Common to Both Presses

The suspension of the top entablature is a special feature by which it is possible to dispense with the nuts or collars on the main columns, which would otherwise be required on the underside of the top entablature. The entablature is held in position by means of forged steel bolts and by small crossheads mounted on special springs. The springs, which compensate for any undue shocks imposed during forging operations, are seated in the tops of the columns. A locating peg passes through each small crosshead and spring into the column. As the top tie bolt nuts are tightened, the entablature is lifted hard against the bottom faces of the top column nuts.

Another unique feature is the manner in which the four columns rest on two stools located in the press foundation pit. Recessed pads are fitted into the stools that accept the columns, and these stools can be adjusted in height by means of taper wedges, so that, in the event of any settlement of the foundation, the press can very easily be relevelled. It should be noted that if adjustment is necessary, the weight of the press will have to be taken by hydraulic jacks.

The press is secured to the foundation by means of four long holding-down bolts, which pass through the base plate and stools to the bottom of two concrete blocks on which the stools are set. Four pockets cut out of these blocks enable inspection of the bottom nuts to be made. The top nuts are on the upper face of the bottom entablature and are accessible for tightening purposes.

The press is fitted with a moving table that is divided into three parts, a centre and two outer portions. The table sections can either be connected together as one table or the two outer tables can be operated independently by special double-acting hydraulic cylinders, a drag bar being supplied for coupling the tables to the hydraulic movement. A series of holes is machined in this drag bar to enable a removable pin to engage in any one of them, thus allowing table travel for the purpose of tool changing and particular forging operations. Two table traversing assemblies are provided on the press, one on the right and one on the left of the bottom entablature, and these can be operated together, if required, by engaging a locking pin on the control levers.

Another unusual feature is the flexible method of securing the slide table beds to the main base. These beds are hinged to the base and are supported on folding keys for about two-thirds of their length. By this method of attachment, the slide table beds are free to move independently of the base ; thus, any possible expansion difference may take place without serious damage to the press.

Each press has a multi-station ejector which can be located in any one of three positions, to facilitate handling during high-speed piercing and die-forging work. Hydraulic table locks are also provided, for the accurate centring of the tables during the carrying out of such work. The ejector comprises three hydraulic cylinders, the large centre cylinder performing the upward stroke, and the two smaller side cylinders making the down stroke. In all three cases, the rams are fixed and the cylinders move, the advantage of this arrangement being that falling scale is deflected away from the working faces of the rams by the cylinder castings. An electrical interlock system ensures that the holes in the table and the drag-bar are in perfect alignment with the ejector push rod before hydraulic movement can be effected.

The moving crosshead is narrow, to allow for a close approach of the handling equipment to the anvils during working. Lubrication of all moving parts is adequately provided by means of mechanical lubricators and grouped nipple assemblies.

The main control valves for the press are operated by Servo systems, which give finger-light sensitive control and enable a high working speed to be maintained without effort on the part of the operator.

Each press is designed for normal or quick forging, depending upon the nature of the work upon which the press is engaged. The difference between normal and quick forging is briefly as follows. Under normal forging operations, on the down-stroke of the press, prefill water is drawn through the prefill valves into the main cylinders from a buffer vessel situated on the top of the press. This prefill water is supplied from a vessel located near to the press at a pressure of approx. 60–70 lb./sq. in. As the high-pressure water is introduced into the cylinders, the prefill valves automatically close for the duration of the pressure stroke. On the up-stroke, the prefill valves open, and water is returned from the cylinders *via* the buffer and prefill vessels to the main supply tank, which is housed on the roof of the accumulator station.

When the quick-forging lever is engaged, the prefill valves are permanently closed, and constant pressure is applied to the underside of the drawback rams ; hence, the full down-stroke is carried out by high-pressure water. The return of water during the upward stroke—which is instantaneous because the drawback cylinders are already charged—is directly through the main control block for the press to the prefill vessel, so that the buffer vessel and prefill valves are by-passed.

HYDRAULIC PUMP HOUSE

The air-hydraulic pressure water plant consists of an accumulator made up of eight air and four air-and-water bottles, together with five high-pressure pump units, and is housed in a two-storey building erected in the stock bay between the two presses. The air bottles are charged to a pressure of 300 atm. by means of a compressor. The pumps are of the horizontal three-throw type, totally enclosed, with an independent oil-pressure supply. Each pump is driven through a reduction unit by a 550-h.p. motor running at 730 r.p.m. Four pumping units are usually in operation, the fifth unit acting as a standby, but the pipework and controls are arranged in such a way that any one of the pumping units may act as spare. The capacity of the accumulator ensures an adequate reserve of pressure water when both presses are working at high speed under full pressure. The

flow of water from the pumps to the accumulator, and from the accumulator to the presses, is automatically regulated in accordance with varying requirements.

Electrically controlled and hydraulically operated valves, which control the supply of the pumps through bypass apparatus, are provided; and the whole system is designed to ensure maximum economy of working under all operating conditions. Adequate safety devices, both audible and visual, are installed, to ensure safe and foolproof working of the whole plant.

FURNACES

All furnaces, the sizes of which are given in Fig. 1, are located in the furnace bay, the reheating furnaces discharging into the forge bay and those of the heat-treatment type discharging into the heat-treatment bay.

The refractory bricks used for furnace construction are of the highest quality and, where possible, hot face insulation bricks have been used, in the interests of fuel economy.

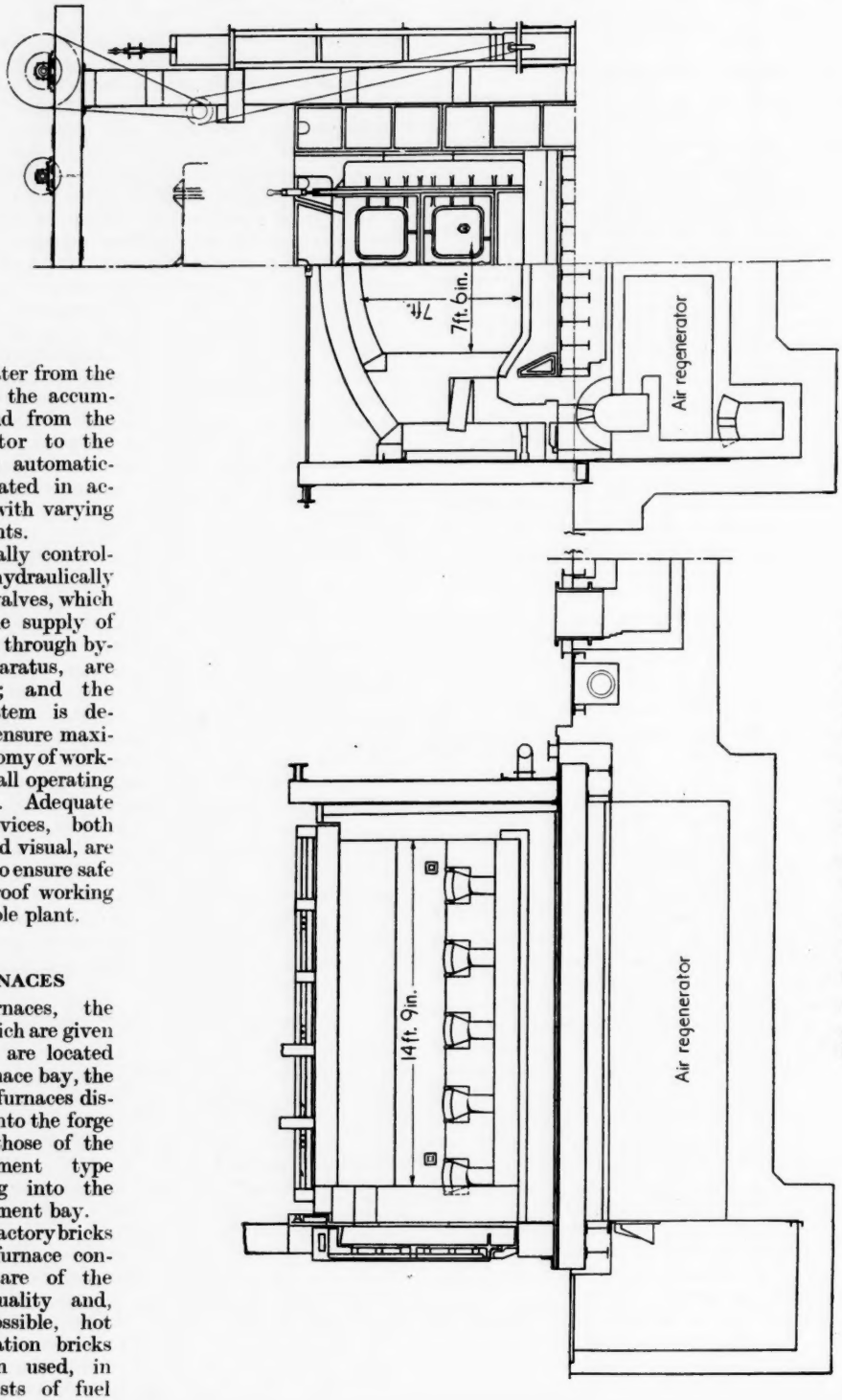

Fig. 2—Sections of fixed-hearth forge furnace

Reheating Furnaces

Eleven reheating furnaces, six being of the bogie-hearth type and the remainder of the fixed-hearth type, have been installed to serve the two forging presses. A furnace of a fixed-hearth type is shown in Fig. 2. Space has also been provided within the main scheme for the installation of further reheating furnaces.

All the furnaces are of the reversing regenerative type, both air and gas being preheated. The air passes through regenerators and the gas through a tubular metallic needle-type recuperator. It will be appreciated that this system of heat recovery gives the conditions necessary for rapid and satisfactory heating of the stock. The reversing equipment is of particular interest. The air/waste-gas valve, which is of the rotary type, has a water-cooled paddle and drum, which enable it to deal with high-temperature exhaust gases with a minimum leakage. Gas reversal is effected by means of water-sealed dipper-type valves. The functioning of this gear is completely automatic, the sequence being electrically controlled to take place at predetermined intervals. From the reversing unit, gas is led to the furnace through lagged mains terminating at the combustion ports, to which air is distributed through underground flues. These combustion ports are arranged alternately, to direct the products of combustion over and under the stock. The furnaces are of robust construction, with the side and back walls enclosed in mild-steel casing, and the fronts and doors constructed in hematite iron castings. All reheating furnaces have a maximum working temperature of 1350° C., the temperature being controlled within the limits of ± 10° C. from 550° C. upwards.

Heat-Treatment Furnaces

The nine furnaces which comprise the heat-treatment section are all of the bogie-hearth type. In many respects, the five larger furnaces resemble

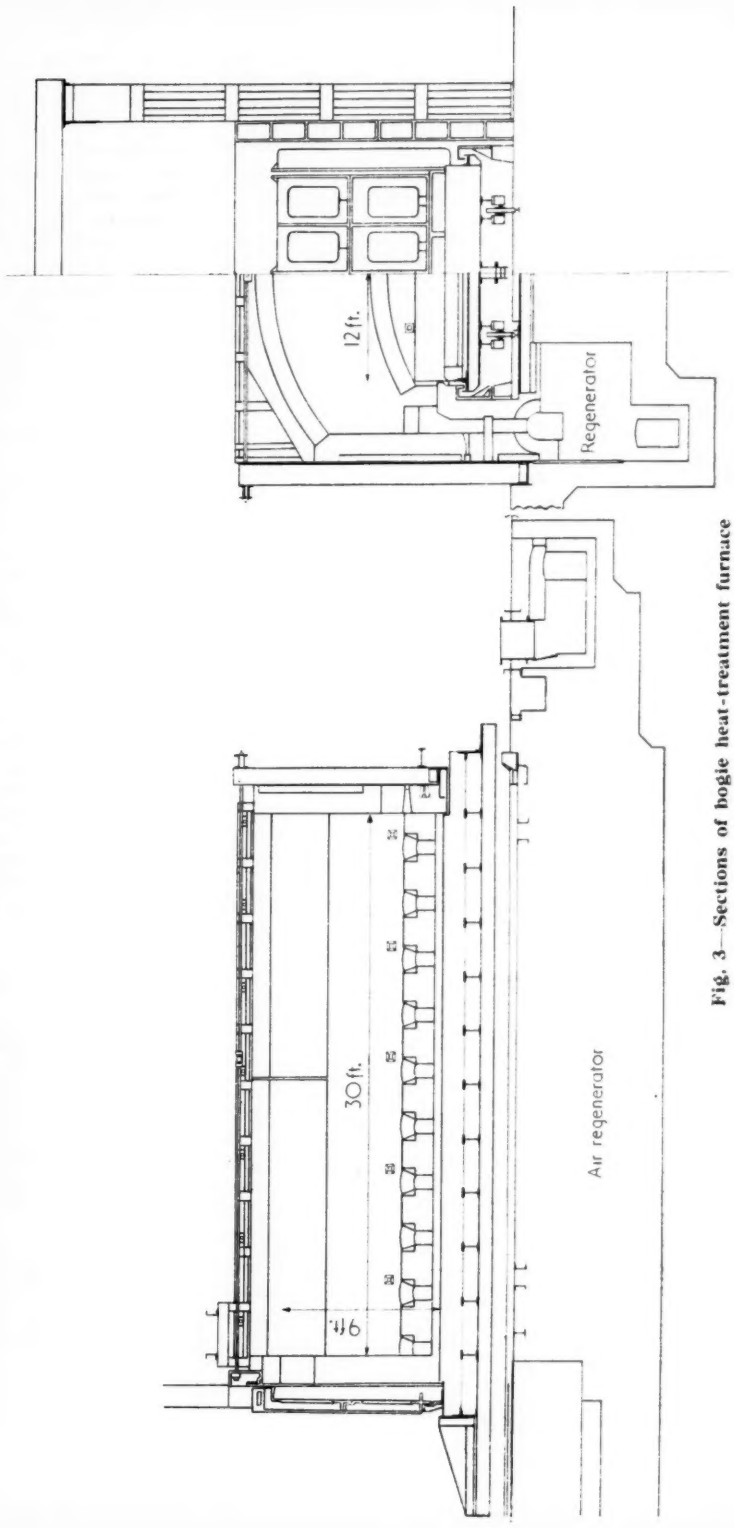

Fig. 3—Sections of bogie heat-treatment furnace

the reheating furnaces, but they are of the air-regenerative type, with similar combustion arrangements and reversing equipment. However, in this case, with lower maximum temperature requirements, preheating of the gas is unnecessary. The construction of a typical heat-treatment furnace of this type is shown in Fig. 3. The bogies, which are constructed from rolled-steel sections, are carried on steel wheels and stub axles, and have an insulated refractory hearth. Particular attention has been given to the sealing arrangements to prevent ingress of air or the escape of exhaust gases. Sand seals are arranged along the full length of each side, and a special bridge construction is adopted in the furnace back wall, to allow an extension of the bogie to pass beneath it and to provide a means of sealing at this point. The maximum working temperature of these five heat-treatment furnaces is 1250° C.

Three tempering furnaces of the recirculation type have been installed for precise temperature control over a range of 100–750° C. The system of heating has been designed to overcome the difficulties experienced at low temperatures in normal types of furnace; namely, the slow heating rate, the inequalities of temperature distribution resulting from local radiation, and the slow-moving convection currents of the gases used.

These furnaces differ fundamentally from the usual type in that, instead of burners being used for heating the work chamber, the heat is generated in a combustion unit that is entirely separate from the furnace proper. To obtain the extreme accuracies and speed of heating at temperatures from 100–750° C., very large columns of hot gases at high velocity are used as the heating medium, and are continuously recirculated by powerful fans through the furnace chamber in a closed system of ducting. Control of the furnace temperature is extremely simple, as it is only necessary to regulate the temperature of this single body of main circulating gases by adding to them the small quantities of fresh gases being burnt in the external combustion chamber.

A further advantage of this system is that the load cannot be heated to a temperature exceeding that of the gases in circulation, the volume of which is such that the heat absorbed by the load represents but a small fraction of the total heat potential being circulated. The result is that the load in the furnace is completely and evenly heated to a temperature which can be controlled to the fine limits of $\pm 3°$ C. This system of heating, as applied to the largest of these three tempering furnaces, is such that the high-velocity gases are recirculated from wall to wall across the furnace chamber, the direction of the flow of gases being automatically reversed at predetermined intervals, so as to apply the heat to the load from each side in turn. This particular furnace is illustrated diagrammatically in Fig. 4.

The furnace combustion chamber has been designed for use with either town gas (500 B.Th.U./cu. ft.) or coke producer gas (132 B.Th.U./cu. ft. gross), together with low-pressure air, and is divided into two smaller combustion units, each being separately fired and provided with a permanently lit pilot flame. For very low temperature work, the furnace can be heated from one combustion unit only.

The furnaces are substantially built for heavy duty, and are well insulated. Circulating fans of the centrifugal type are used. The furnace chamber works under a slight positive pressure, and seals are provided on the doors and bogies, to prevent loss of circulating gases.

The whole furnace combustion system is adequately safeguarded against accidental damage by a series of safety devices that work in conjunction with an electromagnetic gas shut-off valve. These safety devices are wired up to a self-contained floor mounting panel, complete with alarm circuits, starting switches, etc.; and, should the gas supply be cut off for any

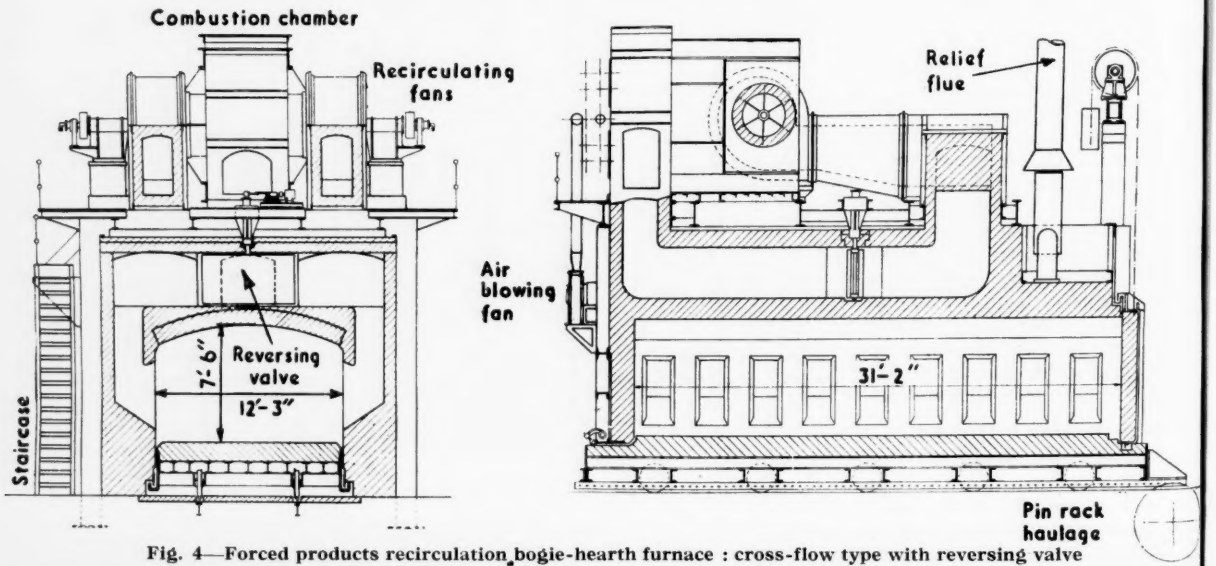

Fig. 4—Forced products recirculation bogie-hearth furnace : cross-flow type with reversing valve

reason, warning lights and an alarm bell bring the fault to the notice of the operator.

The two smaller recirculation-type furnaces use the same principle of recirculation and generally embody the same features of construction as those of the large furnace described above. As distinct from the cross-flow type of heat flow, however, these furnaces are of a more simple down-flow type, without reversing gear, the hot gases entering the furnace chamber through the furnace arch and returning for recirculation through ports at each side of the furnace.

Operating in conjunction with, and of identical size to, the two smaller tempering furnaces is a hardening furnace, designed to operate at temperatures from 550–1250° C. This furnace has been installed for general-purpose work at maximum efficiency over a wide temperature range. The furnace is directly fired by two separate sets of burners, one set firing under the furnace arch, the other set arranged to fire through ports in the bogie hearth, with independent adjustment between top and bottom heating. Recuperation is included for both air and gas : the recuperators are of the metallic needle type, and waste flue gases are exhausted to atmosphere by a positive motor-driven fan. All hot gas and air pipes are adequately lagged to maintain the recuperated heat up to the burners.

As in the case of the tempering furnaces, an electromagnetic gas shut-down valve is included in the mains supply to the furnace, to operate in the event of an air supply failure.

Bogie haulage for both reheating and heat-treatment furnaces is arranged by means of special rack wheels, electrically driven, engaging with pin-type racks that are located centrally underneath the furnace bogies. These haulage units are electrically interlocked with the door-lifting gear, to ensure that the door is in the open position before the bogie can be moved.

Gas Supply

Clean gas of a gross calorific value of 132 B.Th.U./cu. ft. is distributed to the furnaces from a 30-in. overhead ring main around the furnace bay at a height of about 28 ft. above floor level, this main being fed from the Company's own coke producer plant.

Instrumentation

To ensure efficient and economic working of the twenty furnaces, considerable attention was given to the question of instrumentation. The temperature of each furnace is automatically controlled in the following manner.

A thermocouple supplies a very small voltage to an electronic potentiometric temperature-recording controller, this voltage being converted into movement of the gas and air valves by means of a floating proportional regulator and power cylinder. The valves are mechanically linked, and are so designed as to give a constant air/gas ratio under all conditions. Furnace pressure control has been fitted on two furnaces to maintain the pressure inside the furnace at hearth level slightly in excess of atmospheric pressure : this prevents infiltration of cold air into the furnace and the hot gases being expelled other than through their normal channels. Gas and air flow meters have also been provided, the former recording the gas flow together with the total gas consumption, and the latter enabling the operator to check the air/gas ratio. In addition, gas and air pressure gauges are provided.

AUXILIARY EQUIPMENT

Cranes

The building is served by the following cranes : two 40-ton cranes with 10-ton auxiliary hoists in the heat-treatment bay ; one 10-ton crane in the furnace bay, which has been installed chiefly for maintenance purposes ; and one 40-ton crane with 10-ton auxiliary hoist in the stock bay. In the forge bay three special forging cranes have been provided, two being of 75 tons capacity with 60-ton turning gear and separate 20-ton auxiliary crabs, the remaining one being of 40 tons capacity with a 40-ton turning gear and a separate 10-ton crab.

Quenching Facilities

Six tanks, three containing oil, the remaining three of similar size containing water, have been provided in the heat-treatment bay for the purpose of quenching forgings during heat-treatment. Two vertical tanks, the sizes of which are as given in Fig. 1, are completely below ground and are utilized for the quenching of long forgings whose length to diameter ratio is high, so as to minimize distortion during hardening. The remaining four are of the horizontal type.

Electrical Installation

Incoming supply (3-phase, 50-cycle) is received at the forge sub-station, which is housed in the same building as the accumulator plant, at a pressure of 11,200 V. ; it is then reduced to 3300 V. by two 1500-V. kVA. transformers, this being the voltage for the pump motors. The 3300-V. supply is then reduced by two 500-kVA. transformers to 400 V., which is the standard for all smaller motors in the shop.

The cranes operate on a 230-V. D.C. supply, provided by a 500-kW. arc rectifier unit.

The main shop lighting is of the latest type used, and is a combination of mercury discharge and incandescent filament lamps with suitable reflectors ; fluorescent lighting has been employed in the hydraulic pump house.

Water Services

An adequate water supply is available for the necessary hydraulic service, and for quenching and cooling purposes. Both clean and river water are installed, the former being used for the accumulator plant and the presses, and the latter used for quenching purposes and for the cooling of the air and gas reversing valves on the furnaces.

N E W S

ANNOUNCEMENTS AND NEWS OF SCIENCE AND INDUSTRY

THE IRON AND STEEL INSTITUTE

Meeting in Swansea

The Special Meeting of the Institute to be held in Swansea from **7th to 10th October, 1952,** will open with a visit to the Trostre works of the Steel Company of Wales, Ltd., the Minister of Supply being the chief guest. In the evening of the first day the Mayor of Swansea will preside at a Reception to be held in the Brangwyn Hall.

On the second day, visits will be made to the Margam and Abbey works of the Steel Company of Wales, Ltd.; in the evening a Dinner will be held in Swansea.

The third day will be given up to visits to numerous works near Swansea. Excursions are being arranged for Ladies attending the Meeting.

Corrosion of Phosphate Coatings

A meeting will be held at the offices of the Institute at 2.0 P.M. on **Tuesday, 28th October, 1952,** to discuss the following papers, which were published in the *Journal* for January, 1952:

"*Phosphate Coatings as a Basis for Painting Steel* (pp. 10–15)

"*Corrosion by Retained Treatment Chemicals on Phosphated Steel Surfaces*" (pp. 15–18)

"*Tentative Analytical Tests for Phosphate Coatings on Steel*" (pp. 19–20)

together with:

"*2nd Report of the Methods of Testing (Corrosion) Sub-Committee*" (July, pp. 255–272).

President-Elect

The Council has resolved that Mr. James Mitchell, C.B.E., Honorary Treasurer, be nominated at the Autumn General Meeting for election as President at the Annual General Meeting in 1953, to hold office for one year.

Changes on Council

The following have accepted invitations to serve as Honorary Members of Council during their periods of office:

Mr. W. D. JENKINS, President of the Ebbw Vale Metallurgical Society

Dr. W. J. PETCH, President of the Leeds Metallurgical Society

Mr. W. L. JAMES, President of the Lincolnshire Iron and Steel Institute.

Ablett Prize

Captain C. A. ABLETT, O.B.E., has kindly agreed to a recommendation by the Engineering Committee to alter slightly the terms of the Ablett Prize in an effort to increase its popularity.

The following are now the terms of the Prize:

The Prize, value £100, will be awarded annually to the author(s) of the best paper *sent in* each year on a subject associated with iron and steelworks engineering,

The winning paper will be considered for publication in the Engineering Section of the *Journal*.

The author(s) should be below the age of 40 and not in charge of more than one department in the organization wherein he is engaged.

Authors need *not* be Members of The Iron and Steel Institute.

Foreign Members

With the ending of the state of war with Japan on 28th April, 1952, the Council has decided that those of Japanese nationality are now again eligible for membership of the Institute.

NEWS OF MEMBERS

▶ Mr. S. C. ANTHONY has left Henry Wiggin and Co., Ltd., and is now Assistant Works Manager with the Ever Ready Co. (Great Britain), Ltd.

▶ Dr. D. V. ATTERTON has left Cambridge University to take up the appointment of Research and Development Manager with Foundry Services, Ltd., Birmingham.

▶ Mr. G. R. BELL has left F. W. Berk and Co., Ltd., to become Personal Technical Assistant to Dr. W. D. Jones of Powder Metallurgy, Ltd.

▶ Mr. D. BINDLEY has left K. and L. Steelfounders, Ltd., to take up the position of Assistant Metallurgist with the De Havilland Aircraft Co., Ltd., at Christchurch.

▶ Mr. F. H. BROOKS, General Works Manager of the Wellman Smith Owen Engineering Corporation, Ltd., has been made a Director of the Company.

▶ Mr. D. J. BULLIVANT has left Deutsch and Brenner, Ltd., Birmingham, to take up the appointment of Foundry Manager with William Redfern, Ltd., Manchester.

▶ Mr. T. A. COSH has resigned the appointment of Works Metallurgist to Jarrow Tube Works, Ltd., and has joined the Research and Development Division of the British Steel Founders' Association, Sheffield.

▶ Mr. D. K. COUTTS has left the Indian Iron and Steel Company, Ltd., and has returned to the United Kingdom.

▶ Mr. A. CROSBY has left the Tin Research Institute, Greenford, and has taken up an appointment as Deputy Chief Metallurgist at the Ministry of Supply's Royal Ordnance Factory, Eccles.

▶ Dr. R. T. FOWLER has left the British Iron and Steel Research Association, London, to take up the post of Lecturer in Chemical Engineering at the University of Sydney, Australia.

▶ Dr. J. GRAHAM has taken up an appointment as Chief Metallurgist with the Marconi Wireless Telegraph Co., Ltd., Chelmsford.

▶ Mr. G. E. D. HALAHAN, formerly Chief Labour Superintendent of the United Steel Companies, Ltd., has been appointed General Works Manager of the Steel, Peech and Tozer branch at Rotherham.

▶ Mr. G. JEFFORD is now in the Geological Survey Department at Kaduna Junction, Northern Nigeria.

▶ Mr. ANDREW JOLLIE, formerly General Works Manager, has been appointed General Manager of the Steel, Peech and Tozer branch of the United Steel Companies, Ltd., at Rotherham, in succession to Mr. H. E. Wright.

▶ Mr. L. V. NEWMAN has been made an Associate Member of the Institute of Mechanical Engineering.

▶ Mr. P. K. PAUL has left Germany and has taken up an appointment with the National Iron and Steel Company, Ltd., Belur, India.

▶ Mr. M. PRESTON has relinquished his appointment as Research Metallurgist with Wm. Jessop and Sons, Ltd., Sheffield, to join the staff of B.I.S.R.A. at Sheffield.

▶ Mr. V. A. SHARP has been appointed Chief Metallurgist to the Melbourne, Australia, branch of the National Forge Pty., Ltd.

▶ Mr. R. L. STUBBS, of the Zinc Development Association, was awarded the O.B.E. in the Birthday Honours List.

▶ Mr. H. E. WRIGHT is retiring from the position of General Manager of the Steel, Peech and Tozer branch of the United Steel Companies, Ltd., at Rotherham, on 30th June, 1952, after 38 years' service. He is remaining with the Companies in a consultative capacity, and will continue to serve on the boards of the associated companies of which he is a director. He is also to supervise the development of commercial research at the Head Office.

▶ Mr. K. H. WRIGHT has been awarded the Institute of British Foundrymen's British Foundry Medal and Prize.

▶ Mr. P. WRIGHT, Assistant Works Manager of Samuel Fox and Co., Ltd., has been appointed Superintendent Rolling Mills at Steel, Peech and Tozer, Sheffield.

Obituary

Mr. H. T. BRADBURY, of the Effingham Steel Works, Ltd., Sheffield, on 30th January, 1952.

Mr. MORRIS SCHRERO, Technology Librarian of the Carnegie Library of Pittsburgh, Pennsylvania, U.S.A., in September, 1951.

Dr. Ing. G. VANZETTI, of the Fonderie Acciaierie Milanesi Vanzetti, at Milan on 5th March, 1952.

IRON AND STEEL ENGINEERS GROUP

19th Meeting—Change of Date

The nineteenth meeting of the Group will be held in London on **Thursday, 30th October, 1952,** and not on 15th October as previously announced. The meeting is to be devoted to the discussion of two papers on Continuous Hot Mills.

BRITISH IRON AND STEEL RESEARCH ASSOCIATION

Physics in Industry Exhibition

The Association took part in the exhibition organized by the Institute of Physics at the Royal Technical College, Glasgow, from June 24th to 28th. This coincided with the Institute's conference on "Physics in the Transport, Shipbuilding, and Engineering Industries."

High-speed stereoscopic films taken through specially installed tuyere windows in several blast-furnaces were shown, and the method of analysis by which the ranges and paths of individual coke and ore particles are plotted was demonstrated. There were three other working exhibits on the stand: a plate thickness meter for measuring thicknesses up to ¼ in. when only one side is accessible; the prototype of a new coating thickness gauge, which measures tin coating thickness from 20–1000 μ-in.; and the Barber disappearing-filament optical pyrometer. Also on the stand was a 300-ton loadmeter with a display to demonstrate its installation on a mill and to explain the principles of automatic gauge control by strip tension.

AFFILIATED LOCAL SOCIETIES

Leeds Metallurgical Society

The recent metal shortage has introduced many serious problems in industry, particularly with regard to the use of alternative materials. Although the position is changing now with respect to some base metals, certain strategic metals are likely to be scarce for some time. To enable information to be exchanged the Leeds Metallurgical Society proposes to hold a Week-End Conference on:

"Problems arising from Metal Scarcities and the use of Alternative Materials"

The Conference will be held at a very attractive venue within two miles of Leeds City Centre, commencing Friday evening, 5th September, and finishing Sunday afternoon, 7th September. This project has the support of the Metal Economy Committee, Ministry of Supply, and a number of speakers of national standing will be present to initiate and take part in the various discussions.

Certain sessions have been reserved for discussion of problems that are experienced by local industries. Some suggestions for these subjects have included: Heat-treatment of alternative En steels; alternative protective coatings; substitution of non-metallic materials; scrap recovery.

It is particularly requested that those interested indicate any problems which are causing particular concern.

All interested in the use of metals in the engineering and allied industries are cordially invited to attend the conference, and it is hoped that the younger technicians will come along. The cost of meals and sleeping accommodation at the Training College will be approximately 35*s*. and there will be a small registration fee. Accommodation for part of the time can be arranged, and meals will be available for those not requiring sleeping accommodation.

All enquiries should be addressed to: Dr. K. J. Irvine, Department of Metallurgy, The University, Leeds, 2.

NEWS OF SCIENCE AND INDUSTRY

Foundry Prize of Sheffield University

As announced in the News Section last month, the degree of B.Met.(Foundry) will no longer be awarded to students at the University. Decisions about examinations made by the Department of Metallurgy have made it difficult to assess students for The Iron and Steel Institute Prize in terms of their performance in "Iron and Steel" and "Melting and Casting." It has been agreed, therefore, that the Prize should be awarded to the student who, in the year of the award, has given the best performance in "Production Metallurgy." This term embraces the subjects of extraction metallurgy, refractories, metallurgical analysis, melting and casting, working processes, properties of alloys, and mechanical testing.

The United Steel Companies, Ltd.—Swinden Laboratories

Members of Council of The Iron and Steel Institute and of other similar organizations were the guests of the United Steel Companies, Ltd., on 24th June, 1952,

when the newly completed Swinden Laboratories at Rotherham were inspected.

Iron and Steel Productivity

The report of the Iron and Steel Productivity Team which, under the leadership of Sir Charles Goodeve, F.R.S., visited the U.S.A. in 1951, ha now been published. The detailed survey of the organization and methods of the American iron and steel industry is combined with and related to an even more detailed study of the industry in Britain, so that direct comparison can be made.

The high productivity of the U.S. industry is attributed to the higher quality of the raw materials, the larger sizes of the plants, and the faster driving of them in the U.S. as compared with the same factors in Britain. Yet in spite of Britain's greater difficulties she holds a leading position as a producer of cheap steel. To reduce costs still further by the combined efforts of the steel, coal, transport, and capital equipment industries is a major recommendation of the Team. Most of the Team's recommendations as to sizes and layouts of plant and equipment appear to be already implemented by the industry's first development plan, now nearing completion.

The report is divided into three main sections dealing with: (*a*) The general structure and the productivity of the industry in the two countries, and including the principal conclusions and recommendations; (*b*) technical details of the processes of ironmaking, steelmaking, rolling, and fuel and refractories; and (*c*) with labour, services, and financial structure. Appendixes give details of labour practices and training in the United States.

Copies of the report (price 5*s*., post free) may be obtained from the Anglo-American Council on Productivity at 21 Tothill Street, London, S.W.1, or from the B.I.S.F. at 11 Tothill Street, London, S.W.1.

National Physical Laboratory Annual Report 1951

The progress of the varied work of the National Physical Laboratory is described in the Annual Report for 1951, which has been published for the D.S.I.R. by H.M.S.O., price 3*s*.

The most important change during the year was the transfer of most of the Engineering Division to the Mechanical Engineering Research Organization at East Kilbride. Another change was the closing down of the Statistics Section of the Mathematics Division. This was necessary to enable the Division to concentrate on the A.C.E. and the new differential analyser.

The Report contains details of the year's work from each Division of the Laboratory.

Nickel–Chrome Alloys

Nimonic 95, a new alloy designed to improve the performance of gas turbines, has been developed in the Birmingham research laboratories of the Mond Nickel Company, and will soon be available. It is similar to Nimonic 90, but has an increased content of hardening elements and provides the same level of strength at operating temperatures 50° C. higher than those at which Nimonic 90 is used.

Surface Hardening of Steel

The Peddinghaus oxy-town-gas system of flame hardening, recently introduced into this country by Surfard Ltd., has been further advanced for use in the surface hardening of steel.

Peddinghaus have designed special burners and produced a comprehensive series of automatic machines to treat a wide variety of components. Their process involves the rapid heating of the steel surface to the hardening temperature, and quenching the heat before it has penetrated below the depth of hard case required. Precise control of temperature is achieved by a new automatic instrument, the 'Milliscope,' which responds to extremely rapid changes of temperature.

Birlec Jubilee

A luncheon was held at the Queen's Hotel in Birmingham on May 7th, 1952, to celebrate the Silver Jubilee of Birlec, Ltd. In an address, Mr. J. H. Crossley, Sales Director, traced the history of the company, formerly known as Birmingham Electric Furnaces, Ltd. The company began as part of Henry Wiggin and Co., Ltd., and was now a part of the International Nickel organization. Since its foundation, Birlec Ltd. has pioneered in furnace design and heating applications over a wide field, ranging from annealing to cremation. Among the more outstanding Birlec products are the rotary drum annealing furnace, the duplex nitrider for aero-engine crankshafts and levers, and the malleable annealing equipment. Employees of the company celebrated the Jubilee, which actually fell on 20th June, with social activities held in the previous week.

New Lubricator for Heavy Plant

C. C. Wakefield and Company have introduced an automatic greasing lubrication battery to meet the precise lubrication needs of large plant such as roll mills in steelworks. It is unusually compact, and—although entirely new in layout—its design and operation are very straightforward.

The first model has been operating at the Appleby-Frodingham Steel Company, Scunthorpe, since November, 1951.

TRANSLATION SERVICE

(The previous announcement was made in the July, 1952, issue of the *Journal*, p. 312.)

TRANSLATIONS AVAILABLE

No. 449 (French). J. COURTHEOUX: "The Rolling of Angles." (*Centre de Documentation Sidérurgique, Circulaire d'Informations Techniques*, 1952, vol. 9, No. 4, pp. 534–542).

No. 450 (German). E. MEIER-CORTÉS: "Experiences with a Box-Type Roof on a 40-ton Open-Hearth Furnace." (*Stahl und Eisen*, 1952, vol. 72, Jan. 3, pp. 10–12; discussion, p. 12).

No. 451 (German). W. LANGE: "Development and Experiences with Basic Chrome-Magnesite Roofs on Large Tilting Open-Hearth Furnaces." (*Stahl und Eisen*, 1952, vol. 72, Mar. 13, pp. 284–287; discussion, p. 287).

TRANSLATIONS IN COURSE OF PREPARATION

The purpose of this announcement is merely to give advance notice of the intention to prepare translations, and orders should not be sent in until a further announcement appears under "Translations Available."

(German). H. VOLLMACHER: "Deformation Ratios in the Thyssen Method of Rail Calibration." (*Stahl und Eisen*, 1952, vol. 72, May 22, pp. 611–616).

CHARGES FOR COPIES OF TRANSLATIONS—The charge for translations is £1 for the first copy and 10*s*. for each additional copy of the same translation. Requests should be accompanied by a remittance. These translations are not available on loan from the Joint Library.

TRANSLATIONS PREPARED AT MEMBERS' REQUEST—Members requiring translations of foreign papers are invited to communicate with the Secretary, who will ascertain whether they can be prepared for inclusion in the Series.

ABSTRACTS OF CURRENT LITERATURE *and* BOOK NOTICES

IRON AND STEEL MANUFACTURE AND RELATED SUBJECTS

CONTENTS

	PAGE
Mineral Resources	423
Ores—Mining and Treatment	423
Fuel—Preparation, Properties, and Uses	423
Refractory Materials	425
Blast-Furnace Practice and Production of Pig Iron	425
Treatment and Use of Slags	426
Production of Steel	426
Production of Ferro-Alloys	427
Foundry Practice	427
Heating Furnaces and Soaking Pits	428
Heat-Treatment and Heat-Treatment Furnaces	428
Forging, Stamping, Drawing, and Pressing	428
Rolling-Mill Practice	429
Welding and Flame-Cutting	430
Cleaning and Pickling	431
Protective Coatings	431
Properties and Tests	432
Metallography	439
Corrosion	441
Analysis	443
Economics and Statistics	444
Miscellaneous	444
Book Notices	445
New Publications	448

MINERAL RESOURCES

General Considerations on the Deposits of Iron-Bearing Minerals and the Evolution of the Metallurgical Industry in Luxembourg. M. Lucius. (*Rev. Tech. Luxembourg*, 1952, **44**, Jan.–Mar., 1–8). A geological survey is made of the most important ore fields and iron-bearing minerals in Luxembourg; the theory of their formation is briefly discussed. Details are given of the ore reserves with estimates of their probable extent. Development of some low-grade deposits (less than 25% Fe) would be economic if beneficiation methods were adopted. An historical survey is made of the steel industry of Luxembourg.—B. G. B.

Iron-Bearing Strata of Anjou-Bretagne. (*Echo Mines*, 1952, Mar., 176). The iron-bearing strata associated with sandstone in Anjou and Basse-Bretagne are described. As much as 600,000 tons of ore per year have been produced from this region. The ore contains more than 50% iron and 15–21% SiO_2.—T. E. D.

The Manganiferous Iron Ore Deposits of Mackamezö in Nordsiebenbürgen, Hungary. F. Kirnbauer. (*Berg- hüttenmänn. Monatsh.*, 1942, **90**, Apr., 47–48). The exact geographical location of the deposits is first described. This is followed by a historical survey of mining in this area since about the sixteenth century. Finally the geological conditions and ore deposits in the area are described.—R. J. W.

ORES—MINING AND TREATMENT

Problems in Sinter Production: Modern American Techniques. (*Iron Coal Trades Rev.*, 1952, **164**, Mar. 21, 653–656). This article reviews recent American experimental work on the sintering of iron ores and discusses modern sinter practice, as indicated by recent conferences of the Amer. Inst. Min. Met. Eng. Reference is also made to Swedish work.—G. F.

Relation between the Fine Structure of Materials and Their Behaviour in Flotation Processes. W. K. Finn. (*Glückauf*, 1952, **88**, Apr. 12, 383–385).

The Economic Importance of Iron Ore Beneficiation. W. Luyken. (*Berg- hüttenmänn. Monatsh.*, 1942, **90**, Feb. 15, 15–22). An introduction is given to methods of beneficiating iron ores, together with amount of iron loss associated with each method. With the help of beneficiation, many raw ores can be used which would otherwise be useless. Besides this, ores containing additions of metals such as copper and manganese can be fully exploited. A further advantage of special importance is the considerable saving of coke resulting from beneficiation. Transport costs are reduced by beneficiation on the spot and subsequent transportation of the concentrate.—R. J. W.

New Beneficiation Problems. A. Götte. (*Metall u. Erz* 1940, **37**, Sept., 350–357). Examples of modern manufacturing problems are illustrated by important practical questions on sorting, crushing, classification, and draining. The applications to the preparation of ores are emphasized. The rapid settling tank, especially the pulsating settling machine, is discussed together with flotation methods and foam destruction (including ultrasonics). The 'float and sink' method is used for non-sulphides. New uses for grinding mills, tube mills, and rod mills are discussed. The limited application of dry crushing methods is pointed out.—R. J. W.

The Present Position and the Prospect of Electrostatic Beneficiation. A. Grumbrecht. (*Metall u. Erz.*, 1940, **37**, Sept., 357–363). The development and the present state of the use of static electricity for the separation and classification of ores and coals in Germany and the U.S.A. are discussed. The methods are particularly applicable to the removal of unwanted minerals in ores. The experiments carried out in recent years at the Bergakademie Clausthal on the electrostatic beneficiation of brown coal and other minerals are summarized.

FUEL—PREPARATION, PROPERTIES, AND USES

Statistical Combustion Calculations. W. Boie. (*Feuerungstechnik*, 1942, **30**, July 15, 161–164). For the combustion of solid and liquid fuels a single empirical equation is derived by statistical methods. This gives the calorific value for a large number of fuels and is a considerable improvement on previous work. The scatter of the points on the graphs shown, indicates that, with the exception of acetylene, alcohol, and the ethylene series, the calorific powers of the hydrocarbons are accurate to within $\pm$ 0·5%, for oils and coals within $\pm$ 3·0%.—R. J. W.

Notes on Combustion Calculations. C. E. Knight. (*J. Inst. Heating Ventilating Eng.*, 1952, **20**, Apr., 9–17). Notes dealing with simple combustion calculations based on the pound molecule method of computation as used by chemists show how this method facilitates understanding of the various chemical equations involved.—J. P. S.

A Laboratory Method for Measuring Some Combustion Properties of Solid Fuels. J. A. Dulhunty and B. L. Harrison. (*Fuel*, 1952, **31**, Apr., 220–225). Problems in the investigation of relations between combustion properties of coal and its fundamental chemical and petrological constitution are discussed, and experimental technique and apparatus designed for the quantitative study of combustion properties are described. The combustion characteristics of coal are fundamentally related to variations in constitution.—J. P. S.

Flame Radiation and Furnace Efficiency. M. Davies.

(*Murex Review*, 1952, **1**, 10, 233–238). The author discusses the design of the experimental furnace constructed at the Royal Netherlands Steel Works. The furnace was contructed for an international project (by France, Great Britain Holland, and Sweden) to help in deriving a theory of heat transmission and in the establishment of laws of luminous flame radiation.—J. P. S.

Flame Propagation: the Measurement of Burning Velocities of Slow Flames and the Determination of Limits of Combustion. Sir Alfred Egerton and S. K. Thabet. (*Proc. Roy. Soc.*, Series A, 1952, **211**, Mar. 19, 445–471). A method of measuring burning velocities of combustible gas–air mixtures near the limits of combustion is developed, using a burner providing a flat disc-shaped flame. The method is applied to methane, propane, *N*-pentane, *N*-heptane, ethylene, acetylene, and benzene flames at velocities of 5 to 10 cm./sec.—J. P. S.

Theoretical Considerations on the Propagation of Flames. I—Speed. II—Inflammability Limits. P. Blanquet and M.-F. Hoare. (*J. Chim. Phys.*, 1951, **48**, Sept.–Oct., 399–406). Formulæ obtained allow the calculation of the variation of flame speed with the initial temperature, pressure, specific heat, thermal conductivity, and composition of mixtures. The facts that flame speeds do not tend to zero as limits of combustion are reached, and that there is a lag between the composition for maximum flame temperature and maximum speed of propagation are explained. The largely mathematical treatment also allows the interpretation of the shape of the curves of the inflammability limits in connection with those of the regions of auto-inflammability. (23 references).

Notes on Heat Exchangers. A. Huet. (*Rev. Tech. Luxembourg*, 1952, **44**, Jan.–Mar., 29–33). A discussion on the heat exchange between fluids flowing through pipes is given and some tubular exchangers are described.—B. G. B.

Approximative Formulae in the Theory of Thermal Regenerators. B. H. Schultz. (*Appl. Sci. Res.*, 1952, **3A**, 3, 165–173). The application of Hausen's theory for the temperatures and efficiency of regenerators involves very laborious computations. It is shown that for some limiting cases more simple formulæ can be derived.—R. A. R.

Thermal Aspects of Furnace Design: Developments in the Application of Heat Transmission to Furnaces. C. Hulse and R. J. Sarjant. (Institute of Fuel and Institute of Petroleum: *Iron Coal Trades Rev.*, 1952, **164**, Feb. 29, 469–477; *J. Inst. of Fuel*, 1952, **25**, May, 94–102). The authors review recent developments in the application of heat-transmission laws to industrial furnaces, and consider the simultaneous solution of equations covering direct heat transfer to the charge and to the furnace structure, heat conduction into the wall, and radiant heat exchange between the charge and furnace structure. The rôles of convection and gas radiation are compared in an attempt to provide a basis for evaluating the relative contributions of these separate mechanisms in terms of local gas velocities and other pertinent factors.—G. F.

Methods of Reducing Gas Consumption in Industrial Furnaces. W. Heiligenstaedt. (*Gas- u. Wasserfach*, 1942, **85**, Dec. 19, 580–583). The present practice of furnace building and design does not yield the best use of the energy supplied. Technical instruction can provide a better approximation to the ideal. The technical methods of reducing gas consumption are by automatic control to ensure correct burning, draught control, heat and gas densities of the furnaces, and the preheating of the air. Careful measurement of all gas and air flows must be the aim of heat technicians. Very considerable saving of gas can be achieved, especially in large and medium-sized furnaces if due attention is paid to these factors.

Method of Determining the Dynamics of Shrinkage of Coals During Coking. A. E. Bresler. (*Zavodskaya Laboratoriya*, 1950, **16**, 3, 291–297). A dilatometric method for the continuous measurement of coal shrinkage during coking and its use for the investigation of some coals are described.—V. G.

Coking Tests with Coal Mixtures. W. Demann and A. Adelsberger. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1941, **4**, June, No 8, 152–161). The experimental furnace used for the coking tests is first described. Experiments are reported in which the effect of coking a good baking coal with coke dust is compared with the effect on a coal of low baking capacity. Furthermore, the coking of mixtures of coal of good baking quality with black and non-baking semi-bituminous coals is described. The effect of the duration of coking on the Ilseder number, and the coke strength is shown graphically for the various mixtures. Also the effect of the proportion of each coal on the Ilseder number and the compression strength is described.—R. J. W.

The Recent Technical Development in Coke-Oven Practice. W. Fitz. (*Feuerungstechnik*, 1942, **30**, May 15, 113–117). Numerous recent advances in coking techniques are described. Amongst these, the necessary plant for the coking of pitch and tar is discussed together with the advantages of such coking. The purification and cooling of the exit gases are described, particular attention being paid to the drying and the removal of naphthalene. The recovery of water from coke-oven gas in various parts of the world is described. The fine dust content (slack) of coking coal and the production of coke dust leads to a discussion on the gasification of such powdered material.—R. J. W.

The Position of the Coking of Coals According to the Latest Experience. W. Studemund. (*Gas- u. Wasserfach*, 1944, **87**, Feb., 37–41). The chemical and physical aspects of problems of the coking of coals are presented, together with the difficulties incurred in the present process. Such phenomena as the expansion pressure, the plasticity, the swelling and the degasification process, and their relation to one another are described. Deductions that may be drawn from works practice are given. Finally, the question of the mixing and crushing of coals is discussed.—R. J. W.

New Aspects of the Question of the Influence of the Milling and Mixing Plant for Coking Coals on Coke Quality. A. Jenker. (*Glückauf*, 1952, **88**, Apr. 12, 363–367). The effect of the proportions of constituent coals in coking coals on coke strength, and the design of milling and mixing equipment based on petrographic considerations, are discussed. Peculiarities of design of several mills and mixers now in operation, introduced for improving coke quality, are explained.—P. F.

Influence of Moisture Content of Coking Coal on Efficiency of Use of Coking Capacity. B. Hofmeister. (*Glückauf*, 1952, **88**, Apr. 12, 367–370). Present water content of German coking coal, 7·0–12·3%) is considered too high, a mean value of 6% being recommended as technically and economically attainable. Methods of reducing the moisture are discussed.—P. F.

A New Dry Cooling Plant for Coke. H. Siebel. (*Gas- u. Wasserfach*, 1944, **87**, Mar. 30, 61–67). Working diagrams are given showing the mode of operation of a new dry-cooling installation for coke. This provides a heat-recovery plant which effects considerable saving in the use of fuel in gas-works and coking plants. It is a big advantage if used in conjunction with an air ventilation system. The dry cooling compares well with a wet-quenching plant from a managerial and coke technicians' viewpoint and also with regard to the space occupied. Economic calculations are given showing the profit that can be expected by its use.—R. J. W.

Cooling Gas with Steam. F. Rosendahl. (*Gas u. Wasserfach*, 1943, **86**, March 13, 128–130). A short article describing plant for coking installations for cooling gases with steam. Diagrams are shown for single and two-stage installations, and the advantages of this type of cooling over the more conventional methods are described. This cooling comes before the ammonia and benzole washers. Performance figures are given.—R. J. W.

Instruments for the Automatic Recording of the Pushing of Coke Ovens and Gas Retorts. H. Siebel and K. Stosiek. (*Gas- u. Wasserfach*, 1940, **83**, Oct. 5, 499–500). Electrical controlling apparatus is described; this works by remote control, by which automatic recording of the discharge times of the different ovens is possible. Such apparatus has the big advantage that by eliminating the personal factor, operations are carried out at regular intervals, thus considerably increasing the oven life.—R. J. W.

Testing the Mutual Solubility of Tar Oils. J. Plückthun. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1942, **5**, Jan., No. 2, 23–30). The percentage solubility of heavy, medium, and anthracene oils in each other has been investigated and the results clearly shown graphically. These oils often contain certain crystalline materials such as naphthalene. The mutual solubility of one oil in another was often found to be only slightly influenced by the presence of up to 15–20% of naphthalene or anthracene. The experimental results obtained are confirmed on a large scale and are of considerable value to the user of fuel oils.—R. J. W.

Bauer's Method of Coal Distillation for Controlling Coke-Oven Operations. K. Scheeben. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1941, **4**, June, No. 8, 183–192). The

performance of Bauer's apparatus for the distillation of coals is described. By correlation of the results obtained with this apparatus over many years with the works analysis from coke-oven plant, many useful results are obtained. Suggestions can be made, at which point in an installation an improved output can be achieved, due reference being made to the state of the plant. The production of by-products is considered. Comparison between Bauer's method and the works process provides a useful means for supervising the works procedure.—R. J. W.

Physical-Chemical Investigations of the Washing of Benzole with Coal Tar Oils. F. Müller, F. Freude, and P. Kaunert. (*Gas- u. Wasserfach*, 1940, **83,** Oct. 19, 521–527). The determination of the physical properties, such as boiling point density, mean molecular weight and variation of viscosity with temperature (using a Höppler viscometer) is described for three oils of molecular weights 150, 181, and 201. The chemical characteristics of the benzole by-product were observed with a Gruppen hydrocarbon analyser. The suitability of oils of various ages for washing benzole was tested by measuring the vapour pressure exhibited by a 2, 4, and 6% solution of the benzole by-product in the investigated oil. Comparison of the measured results with Planck's law established that increasing the age of the washing oil increased the molecular association shown.—R. J. W.

New Means of Producing Gas of Low Calorific Value from Bituminous Coal. F. Nistler. (*Glückauf*, 1952, **88,** Apr. 12, 346–349). A description is given of the performance and design of pulverized coal combustion chambers producing a low-grade fuel suitable for coking. These were developed by the Ruhrgas A.G. after 1949, on the basis of earlier developments by the Hibernia A.G. which were interrupted by the war. Economic and technical aspects are discussed.—P. F.

Cracking of Hydrocarbons in the Coke Oven. W. Ruschmann. (*Glückauf*, 1952, **88,** Apr. 12, 358–363). Experiments carried out in recent years in Germany on the cracking of waste oils and aromatic by-products in coke ovens are described, and the yields tabulated. Oils are sprayed into the hot coke or are initially mixed with the coal before coking. Apart from small quantities of benzene and tar, a high yield of hydrogen-rich gas is obtainable.—P. F.

The Changes in the Properties of Coke caused by Post-heating to High Temperatures. D. G. Wilde and E. Daub. (*Mitteilungen der Kohle- u. Eisenforschung*, 1939, **2,** June, 3, 109–139). Further changes in the composition of a variety of cokes and in the fine structure of the carbon have been found by post-heating to 1200° and also to 1750° C. With increasing temperature, the burning loss and electrical resistivity decrease, whilst the specific gravity increases. The changes were very different for different cokes. It was established that the oldest original coal had the lowest resistivity and the highest specific gravity, and *vice versa* for the youngest. This sequence was retained after post-heating. Investigations using polarized light and X-rays indicate that the coke crystallizes during the after-heating process.—R. J. W.

The Application of Automatic Control to a Gas Producer. M. A. Beechey. (*Instrument Engineer*, 1952, **1,** Apr., 13–16). The paper deals with an approach to the problem of finding a satisfactory method of automatically regulating the coal feed of a Morgan gas producer. This approach is mainly concerned with an analysis of the plant characteristics that affect the control problem. The relative merits of various methods of control are then considered with respect to the results of this analysis.—J. P. S.

Safety Equipment for an Electrostatic Precipitator. W. Maas. (*Rev. Ind. Min.*, 1952, **33,** Feb., 140–141). The high capacity of an electrostatic precipitator (27×10^{-3} microfarads) is sufficient on discharge to ignite flue dust. To avoid risk the precipitator must be divided into several groups of small capacity isolated from one another by thin fusible sections, thus preventing total discharge.—A. G.

Some Experiences with Gas Holders and Gasometers. W. H. White. (*Gas World*, 1952, **135,** Apr. 5, 342–345). The design of gas-holders is surveyed and a general ' Panel Factor ' is defined, which is applicable to both column and spiral guided holders, and indicates the rigidity of the structure. The lay-out and steps in the construction of a new reinforced concrete underground tank, 153 ft. in dia. by 34 ft 6 in. deep, for a 2,000,000-cu. ft. 4-lift spiral guided gas-holder for the North Thames Gas Board is described. Some items of importance in anti-freezing equipment are mentioned.—T. E. D.

REFACTORY MATERIALS

Refractory Applications for Steelworks and Foundry Materials. M. Guédras. (*Mét. Constr. Méc.*, 1952, **84,** Feb., 87–88). The uses of ' Refractolith ' (a graphitized aluminium silicate containing no organic matter) are listed. The preparation of a ladle lining containing 40% Refractolith, 5% colloidal clay, 50% used silica sand, and 5% sodium silicate containing 36% colloidal clay, and the method of lining the ladle are described. Other applications are linings for cupola runners and fore-hearths.—R. S.

Lining Blast Furnaces with Carbon Bricks. A. Send. (*Stahl u. Eisen*, 1951, **71,** Dec. 6, 1361–1365). The development of carbon linings is reviewed. English and German experience confirms the excellent durability of carbon bricks for hearth and bosh linings. Possible dangers and disadvantages in using them are indicated.—J. P.

Development and Experience with Basic Chrome–Magnesite Roofs on Large Open-Hearth Tilting Furnaces. W. Lange. (*Stahl u. Eisen*, 1952, **72,** Mar. 13, 284–287 : Iron Steel Inst., 1952, Translation Series No. 451). The comparison of chrome–magnesite with silica roofs shows that using present-day techniques on tilting furnaces, the basic is superior to the silica roof. The metallurgical advantages are so great that in future there will be a change from acid to basic linings in order to produce steel of higher purity. Because of the high temperatures possible with the basic roof, care must be taken that the furnace is worked to suit the properties of the rest of the furnace. For example, great attention must be paid to reversal times so as not to melt the checkers. Comparison of construction and operating cost favours the chrome–magnesite roof.—J. P.

Dolomite or " Crespi " Open-Hearth Bottoms. (*Hutnik* (Katowice), 1951, **18,** Dec., 487–491). [In Polish]. Methods of lining open-hearth bottoms are discussed, and various procedures are compared, with particular reference to the Crespi method.—V. G.

Industrial Furnace Insulating Refractories. J. D. Custer. (*Indust. Heating*, 1952, **19,** Jan., 127–132, 140). Insulated furnaces give greater conservation of fuel and the time of heating from the cold, to operating temperature, can be reduced by 80–90%. Thinner walls are practicable and the subsequent reduction in weight allows for the lighter construction of foundations, supports, and door frames. Walls of composite material are more satisfactory for continuously operated furnaces than walls built entirely of insulating firebrick.—B. G. B.

BLAST-FURNACE PRACTICE AND PRODUCTION OF PIG IRON

The Installation of Blast Furnaces at Société John Cockerill, Seraing. L. Halbrecq. (*Rev. Univ. Min.*, 1952, Series 9, **8,** 44–54). Details are given of reconstruction involving the construction of a new blast-furnace with new methods of burden preparation and charging. The new furnace is 5·50 m. in dia. with a volume of 650 cu. m. The usual skips for charging have been replaced by an elevated conveyor belt. A Dwight-Lloyd sinter plant with a capacity of 900 tons/day has been installed.—B. G. B.

Desulphurization . . . Worth Watching. W. W. Austin, jun. (*Steel*, 1952, **130,** Jan. 28, 76–81). Various methods of desulphurizing iron are described in this report. Included is a new Swedish system employing burnt lime and coke vigorously agitated in a rotary kiln with the lime. The results that can be obtained with soda ash and calcium carbonate are shown in charts; magnesite brick linings in the basic cupola are stated to be more effective in reducing sulphur than the acid process; the effects of magnesium and some of its alloys are discussed; the disadvantage of this process is the vigorous reaction.—A. M. F.

Phosphorus–Oxygen Equilibria in Liquid Iron, J. B. Bookey, F. D. Richardson, and A. J. E. Welch. (*J. Iron Steel Inst.*, 1952, **171,** Aug., 392–400). [This issue].

Trends in British Blast-Furnace Practice: Comparisons with American Performance. J. Dale. (*Iron Coal Trades Rev.*, 1952, **164,** Jan. 18, 143–148, 152). The author reviews the trends in blast-furnace practice in this country and makes a general comparison with American furnaces of a similar size. The operation characteristics and data presented are based on furnaces with hearth diameters of 20 ft. or less.—G. F.

Electric Iron-Making. H. Walde. (*Elektrowärme Techn.*, 1952, **2**, Dec., 136–140). The applicability, features, and merits of electric ironmaking furnaces are discussed, and their efficiency is compared with that of standard blast-furnaces.—P. F.

TREATMENT AND USE OF SLAGS

Utilisation of Blast Furnace Slag for Manufacturing Glass. R. M. Agarwal. (*Quart. J. Geol. Min. Met. Soc. India*, 1951, **23**, June, 59–62). The economic aspects of using blast-furnace slag to make glass in India are examined and found promising.—R. A. B.

The Manufacture of Blast-Furnace Slag Wool Without Remelting. G. Naeser and P. Dickens. (*Stahl u. Eisen*, 1952, **72**, Mar. 13, 297–301). A process has been developed in which slag, as run directly from the blast-furnace, is converted to slag wool. The great economic advantages of the new process are savings of remelting, capital, and blowing costs and an improvement in quality since the product has a smaller content of ' pearls ' and has fibres of small diameter. The heat of devitrification has been determined and found to be 54 cal./g.; the safe working temperature of the slag wool is about 750° C. A rapid acid dissolution method has been worked out for estimating the ' pearl ' content of the wool.

PRODUCTION OF STEEL

First Report of a Visit to the U.S.A. to Study Iron and Steel Manufacture. P. M. André. (*Mét. Constr. Méc.*, 1951, **83**, Dec., 957–963; Jan., 7–11). This is an account, with general rather than specific information, of a French productivity team's visit to the U.S.A.—R. S.

The Methods of Producing Steels and Their Properties. K. Daeves. (*Metallwirtschaft*, 1942, **21**, Nov. 27, 715–717). The three important methods of steel manufacture are distinguished and the necessary raw materials and important properties described. By suitable arrangement of the raw materials for the basic and acid Bessemer processes, it is possible to alter considerably the useful range of applications of the resulting steel. Thus, with silicon and aluminium killed special basic-Bessemer steel, and by the development of HPN steel, all the useful properties of open-hearth steels are produced. The electric-arc method must be restricted to the production of the higher-alloy steels and for steels where special properties for working or use are required.—R. J. W.

Trials to Produce Basic-Bessemer Steel Low in Nitrogen and Phosphorus. K. Mayer, H. Knüppel, and H. Pottgiesser. (*Stahl u. Eisen*, 1952, **72**, Feb. 28, 225–232). The method employed at the Dortmund Hörder Hüttenunion A-G. for producing PN steel and the results obtained are reported. Using 99·8% oxygen to enrich the air to 50% oxygen, steels have been produced with nitrogen contents less than 0·003%, the phosphorus and oxygen contents lying in the usual open-hearth steel range. Essentially similar results can be obtained by blowing with oxygen/carbon-dioxide mixtures. A new procedure for producing PN steels employs increased blowing pressure. The age-embrittling action of nitrogen, phosphorus, and oxygen was investigated as a function of the contents of these elements and of heat-treatment. Grain-boundary embrittlement must also be taken into consideration. This depends mainly on the oxygen content and previous heat-treatment. Service behaviour of PN steels as sheets, cold-reduced strip, wire, and structural steels confirms these findings as well as the suitability of the notched-bar impact test for assessing these steels.—J. P.

Effect of Emissivity and Flame Length on Heat Transfer in the O.H. Furnace. M. W. Thring. (*J. Iron Steel Inst.*, 1952, **71**, Aug., 281–291). [This issue].

Metallurgy of Iron, Manganese and Phosphorus Reactions in Basic Steelmaking. E. Witten. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 83–93: Iron Steel Inst., 1952, Translation Series No. 446). From a survey of the literature it is concluded that, for each basicity and temperature, a slag takes up that total quantity of iron plus manganese plus P_2O_5 which suffices to reduce the melting point of the $CaO–SiO_2–Al_2O_3–MgO$ base mixture to just below the working temperature of the slag. The ratio in which the three materials dissolve in the slag depends on the basicity, expressed as $(\Sigma CaO)/[\Sigma CaO + (\Sigma SiO_2)]$ or $(\Sigma CaO)/(\Sigma SiO_2)$, and on the amounts of manganese and phosphorus in the total furnace charge. Slag and metal analyses reported in the literature show that these relationships may be expressed as equilibrium functions and that these are valid for both acid and basic open-hearth and basic-Bessemer practices. In all three processes equilibrium is reached after the first third of the refining period and quickly re-established after any additions. The existence of these equilibrium relationships offers the possibility of calculating slag and bath compositions as functions of basicity, temperature, slag volume, and amounts of manganese and phosphorus. The methods of calculation are illustrated but nomograms have been worked out to render the calculations unnecessary. The influence of basicity, slag volume, temperature, manganese, and phosphorus is discussed by reference to some specific examples and certain conclusions of importance in steelmaking are indicated.—J. P.

Single-Crystal Structure of Skull Removed from an Open-Hearth Bottom. H. Krainer. (*Berg- hüttenmänn. Monatsh.*, 1947, **92**, No. 1–3, 55–56). The chemical, metallographic, and X-ray examination of a piece of solidified metal removed from the bottom of an open-hearth furnace is described.—V. G.

Accurate Methods for Computing Electric Furnace Heats. R. B. Shaw. (*Steel*, 1952, **130**, Jan. 21, 72–75). Examples of calculations for determining the quantities of ferro-alloys to add to electric furnace heats to finish within a specification are given. Two of the methods are approximate but three accurate methods are also given.—A. M. F.

Melting Stainless Steels in the Electric Arc Furnace and Refining with Oxygen. K. Bungardt, E. Pakulla, and K. Tesche. (*Stahl u. Eisen*, 1952, **72**, Feb. 28, 245–255). The metallurgical and economic bases for the production, from scrap, of high-chromium and chromium-nickel steels using pure oxygen refinement have been worked out on 300-kg. heats in an electric-arc furnace. The connection between carbon and chromium contents and temperature as well as the equilibrium constant $K = [Cr]/[C]$ have been determined. The results are in agreement with those of Hilty and of Everard and Brandt. These relationships have been tested on heats made in 10, 20, and 30-ton arc furnaces and found to be valid. In addition, the following were studied: The relationships between chromium recovery, carbon content after refining, and mean carbon drop; between carbon drop, carbon content, and temperature; and between quantity of oxygen employed, mean carbon drop, and mean refining temperature; and the influence of the iron in the slag on the chromium in the slag. Investigations of the oxygen consumption as a function of carbon content before refining, the oxygen efficiency, consumption of lances, life of refractory linings, power savings, and the influence of oxygen refining on the deformability of the steels were also made.—J. P.

Direct Reduction Yields Variable Density Steels. P. E. Cavanagh. (*Iron Age*, 1952, **169**, Jan. 24, 63–68; Jan. 31, 108–111, 114). **Foundation Develops Process for Producing Articles of Steel.** P. E. Cavanagh. (*Blast Furn. Steel Plant*, 1952, **40**, Feb., 220–221). The Ontario Research Foundation has developed a process for producing steel of any desired density and analysis within a very wide range. Dry, fine, prepared ore generally finer than 60 mesh is poured directly into suitable moulds and is then reduced at about 2000° F. It is held for a treatment time of several hours at this temperature. The resulting article has the same composition and structure of normal steel except that it contains a predetermined amount of spherical voids which are not interconnected. The hot working of controlled-density steel, and controlled-density steel as a substitute for iron powder and for light steel products are discussed. Controlled-density steel can be produced with any density between 1·0 and 7·2 directly from the furnace.

The Induction Crucible Melting Furnace for Mains Frequency. R. Lethen. (*Giesserei*, 1952, **39**, Apr. 3, 145–152). Hitherto this type of furnace has been built only with thick walls for melting magnesium. The author describes the recently introduced thin-walled cast and rammed pots. In spite of constructional and electrical difficulties, the furnace has proved successful and is used for melting aluminium, brass, iron, and steel.—J. G. W.

Development of Graphite Electrodes and Study of Heat Losses with Different Electrodes in the Single Electrode Inert-Atmosphere Arc Furnace. W. E. Kuhn. (*J. Electrodep. Tech. Soc.*, 1952, **99**, Mar., 97–108).

Self-Tightening Ingot Grippers—Static Calculation and Comparison of Four Tongs. F. Leikert. (*Technische Mitteilungen Krupp, Technische Berichte*, 1942, **10**, Nov., No. 3, 39–45). Using the principle of virtual displacement, the locking forces are calculated for four different designs of tongs used for gripping ingots. Calculations indicate that one arrangement of levers is preferable to the others. Tongs of similar weights are compared and the forces calculated for various values of the jaw gap, the locking force, and various angles between the corresponding levers in each design.—R. J. W.

Investigations on Self-Acting Ingot Grippers. F. Leikert. (*Technische Mitteilungen Krupp, Technische Berichte*, 1943, **11**, Mar., No. 1, 7–20). In this paper, modifications are made to the best of the four tongs described in a previous paper ("Self-Tightening Ingot Grippers—Static Calculation and Comparison of Four Tongs") and their performance is discussed.

PRODUCTION OF FERRO-ALLOYS

The Recovery of High-Percentage Manganese Slags from Spiegeleisen. J. Wittig, C. Wens, and H. Wentrup. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1942, **5**, Jan., 37–57). Eight groups of experiments on the recovery of manganese are described. In the first two groups, the Lofquist method of separation is investigated in a gas-fired furnace and in a 120-ton open-hearth furnace. The addition of sulphur to the bath, with and without heating the Spiegeleisen in a converter, and with increasing SiO_2 contents is then described. Experiments are reported on the separation of manganese as manganese sulphide. Finally the various methods of separation are discussed from both economic and technical viewpoints.—R. J. W.

Molybdenum. (*Tisco Rev.*, 1952, **20**, Jan., 14–15, 13). A review is given of the manufacture of ferromolybdenum and molybdenum silicide.—B. G. B.

The Manufacture of Tungsten Powder and Ferrosilicon at the Works of the Broken Hill Pty. Company Limited, Newcastle. I. H. Carne. (*Australasian Institute of Mining and Metallurgy*, 1947, Apr.–May–June, 1–14). The extraction of tungsten from wolframite and ferrosilicon production are described. The plant for making ferrosilicon comprises three 4500-kVA. buried arc furnaces and one 1500-kVA. Heroult tilting furnace, together with the necessary auxiliary equipment. Dimensions and operating details of the furnaces are given. A typical charge for the manufacture of 50% ferrosilicon consists of: Quartzite 2000 lb.; coke 800 lb.; coal 200 lb.; and steel scrap 1000 lb. At the temperature of the electric arc the reaction between the carbon of the coke and coal with the silica of the quartzite results in the formation of silicon and carbon monoxide. The silicon thus formed alloys with the scrap in the charge forming ferrosilicon. Approximately 3000 lb. of ferrosilicon are removed at each cast.—J. P. S.

FOUNDRY PRACTICE

Modern Foundry Practice. T. W. Bushell. (*North East Coast Institution of Engineers and Shipbuilders*, 1952, Mar. 21, Advance Copy). Some of the changes in equipment and in cast materials which have taken place during the present century are briefly reviewed. The making of the 'perfect casting' is considered and, after a description of a recently completed new general foundry department, some of the troubles which have to be overcome in the production of steel castings are discussed. Finally, casting faults, and modern methods of testing and inspection are dealt with.—J. P. S.

Modernization and Mechanization of Foundries. D. Iturrioz. (*Met. y Elec.*, 1951, **15**, Dec., 51–54). [In Spanish]. A list is given of services, plant, and problems to be considered when studying the modernization and mechanization of a foundry.—R. S.

Machinery for the Mechanization and Modernization of Foundries. D. Iturrioz. (*Met. y Elec.*, 1952, **16**, Jan., 28–34) [In Spanish]. Following some remarks on methods of ramming sand, some American moulding machines are described.

Hoppers for Transporting Sand. (*Fonderie*, 1951, July, 2578–2581). Several types of tilting and open-bottom hopper are described and illustrated.—R. S.

Sandslingers and Their Application. H. Mastalerz. (*Przeglad Odlewnictwa*, 1952, **2**, 2, 47–52). [In Polish]. Types of sandslinger and their operation are discussed.—V. G.

Graphite and Its Application in the Foundry. C. Dennery and F. Pensa. (*Fonderie*, 1951, July, 2547–2564). The authors discuss methods of recognizing graphite and the formation of graphite by: (*a*) Decomposition of carbohydrates; (*b*) heating carbon to high temperatures; (*c*) dissociation of carbides; and (*d*) crystallization of graphite in carbon-saturated alloys. The manufacture of electrodes is described. The following physical and chemical properties of synthetic graphite are considered: Heat resistance and thermal conductivity; electrical resistivity; coefficient of expansion; mechanical properties; density and porosity; resistance to oxidation; and solubility in iron. In the second part, the following applications are described: (1) Crucibles, agitators, moulds, casting runners, ladles, and cores; and (2) additions to moulding sand, carburizing, and ladle additions.—R. S.

The Use in the Foundry of Machine-Cast Pig Iron—Remelting Tests Carried Out with Sand Bed and Machine-Cast Hematite Iron. A. Scortecci, W. Demicheli, M. Drufuca, and A. Palazzi. (*Metal Ital.*, 1952, **44**, Feb., 55–72). After a brief description of the pig-casting machine the authors discuss the advantages and disadvantages of machine-cast and sand-bed methods. Hematite iron produced by the two methods was remelted and cast and the properties compared. It was found that irons from machine-cast pig irons have significantly higher combined carbon and greater tensile strength, although, from an industrial point of view, the differences are not appreciable. No notable differences were found in the other characteristics, especially in the bending, impact, and hardness tests, graphite size, sensitivity to chill, and fluidity. (16 references).—M. D. J. B.

Melting Cast Iron Swarf in Cupolas. (*Engineer*, 1952, **193**, Apr. 11, 503). **Melting Cast Iron Borings in Foundry Cupolas.** (*Engineering*, 1952, **173**, Apr. 11, 459–460). **Cupola Melting of Cast-Iron Borings.** (*Iron Coal Trades Rev.*, 1952, **144**, Apr. 11, 832). **Cupola Injection Process Reclaims Swarf.** (*Machinist*, 1952, **96**, Apr. 12, 561). **Tackling the Pig Iron Shortage, New Method for Charging Borings into the Cupola.** (*Metallurgia*, 1952, **45**, Apr., 199–200). The process developed by Crofts (Engineers), Ltd., for charging borings and turnings, without briquetting, into cupolas is described. The swarf is fed into a sloping chute on the charging platform, at the foot of which a compressed-air-operated ram reciprocates a feed bar. This bar pushes the swarf into the cupola on each forward stroke; at 15 strokes/min. about 15 cwt. swarf are charged per hour. The swarf enters the cupola at a level where the other charged materials are packed sufficiently tightly to prevent the light particles from being ejected by the blast.—R. A. R.

Inoculation of Cast Iron: Use of Calcium Silicide. W. S. Williams. (*Iron Steel*, 1952, **25**, Jan., 9–10, 32). The author describes the use of the 'quasi-bessemerising' process in experiments on the production of nodular cast-iron ingot moulds with calcium silicide inoculation. It is stated that absorption of calcium can be obtained with sulphur contents as high as 0·1% and at temperatures of 1200–1250° C.—G. F.

Mechanical Properties of Cast Steel as Influenced by Mass and Segregation. J. F. Wallace, J. H. Savage, and H. F. Taylor. (*Trans. Amer. Found. Soc.*, 1951, **59**, 223–243). Tensile and Charpy impact tests were carried out on specimens cut from solid and hollow 5-in. dia. low-alloy steel cylinders cast in green-sand moulds. The specimens were heat-treated before machining. From the mechanical test results it may be concluded that: (*a*) Increasing mass reduces the tensile and yield strength appreciably, tensile ductility considerably, and impact resistance only slightly, in the solid cylinders; (*b*) effect of mass on the strength and impact resistance is eliminated and the effect of mass on ductility reduced, in the hollow specimens. Interdendritic segregation and agglomeration of inclusions, shown by microscopic examination and fracture studies, are the cause of these differences.—R. L. B.

Present Trends in the Steel Foundry. J. P. Quenedey. (*Mét. Constr. Méc.*, 1951, **83**, Dec., 979–981). Side-blown acid converter practice is described. The flexibility of this process as regards output, quality, and types of casting produced is discussed. The importance of casting design is stressed. Other trends mentioned briefly are: The combination of castings and weldments; improvement of casting surface by sand- and shot-blasting; and more accurate castings to reduce machining.—R. S.

Works Experience with Low-Frequency Induction Furnaces in Iron and Metal Foundries. H. Kalpers. (*Elekrtowärme*

Techn., 1951, **2**, Dec., 133–135). Performance and economic aspects of induction furnaces with a capacity of up to four tons of iron are discussed. The furnaces are shown to be useful for melting small scrap, and permit fairly exact control of the carbon content. Iron is not directly cast into moulds, but into pigs of definite sizes and compositions which are used to control the composition of cupola melts.—P. F.

Plaster of Paris as Material for the Manufacture of Moulding Plates. K. Schröder. (*Giesserei*, 1952, **39**, Mar. 20, 127–130). The properties of various gypsum mixtures are compared, with reference to compression, bending, and wear tests. The moisture content is found to be the dominating factor, the strength being doubled in the course of one day, and drying continuing for about a week. Great importance is attached to lacquering before putting into use.—J. G. W.

Preparation of Cemented Moulding Sands. H. Gries. (*Giesserei*, 1952, **39**, 20 Mar., 121–127). Arguments in favour of synthetic sands, and particularly of cemented sands, are given. It appears from data of compressive and shear strengths and of gas permeability, that optimum cemented sands should contain between 50 and 80% of used sand. Machinery and installations for preparing cemented sands are described. The costs of sands prepared in various ways are compared.—J. G. W.

HEATING FURNACES AND SOAKING PITS

New Views on the Method of Heating Steel for Plastic Working. E. Terlecki. (*Hutnik* (Katowice), 1952, **18**, Feb., 37–42). [In Polish]. The unnecessarily slow heating rate of steel for plastic working used at present is criticized. The division of steels into three groups, according to the heating rates required, and a general formula for calculating the necessary heating time are given.—V. G.

Examples of Gas-Heated Industrial Furnaces in the Iron, Steel and Metal Industries. O. Wolff. (*Gas- u. Wasserfach.* 1942, **85**, Dec. 19, 575–580). Numerous designs of furnace are described and compared. Furnaces for heating forgings, sheet, and wire are described, together with the various methods of heating (*e.g.*, radiant tube heating). The changing of gas-fired furnaces to oil-firing, the effect on the heat distribution of various burners, the fuel gas, and the exhaust gases are discussed. The use of rotary hearth and other mechanical furnaces results in considerable changes in procedure. The necessity for close control in the modern works is stressed.

HEAT-TREATMENT AND HEAT-TREATMENT FURNACES

Induction Heating for Continuous Heat Treatment of Sheet and Strip. F. C. Hull and H. Scott. (*Metal Progress*, 1952, **61**, Feb., 57–61). The technical knowledge is now available to heat-treat economically and continuously wide strips of non-ferromagnetic metal. Full-scale equipment has been set up and run experimentally at two places in America.

Thoughts on Case Hardening. M. Guédras. (*Mét. Constr. Méc.*, 1951, **83**, Dec., 997–1001). The effects of some elements during case-hardening are described and the various case-hardening mixtures are considered with regard to their properties (heat transfer, and capacity and speed of hardening). Types of case-hardening boxes are mentioned. Eight classes of defect in case-hardened parts are considered.

Ford Automotive Parts Hardened by Dry Cyaniding. (*Indust. Heating*, 1952, **19**, Jan., 26–34, 186). Dry cyaniding of motor-car parts in two hydraulic pusher furnaces followed by an automatic oil quench is described. The furnaces are heated by 12 natural-gas-fired radiant tubes. Details of the operation of the cyaniding process and the composition and hardness of individual steel parts are given.—B. G. B.

The Function of Energizers in Pack Carburizing. A. Hultgren. (*Jernkontorets Ann.*, 1951, **135**, Nov., 575–604). [In Swedish]. Methods of using the energizers K_2CO_3, Na_2CO_3, and $BaCO_3$ in box carburizing have been studied. K_2CO_3 or Na_2CO_3 may be applied as a layer on top of the charcoal. On heating to the carburizing temperature they spread out rapidly, forming a uniform mixture with the charcoal. As $BaCO_3$ remains where it is applied it should be put on as a thin coating on the steel surface, preferably with a binding agent such as lacquer. The coated parts should be packed in charcoal which has been thoroughly washed with dilute HCl. When carburizing with $BaCO_3$ the presence of a little K_2CO_3 in the charcoal or the coating may interfere with the carburizing reaction and lead to poor results. The decline in carburizing power of a repeatedly used carburizing agent is probably caused by a rapid loss in active surface area of the charcoal particles, not by loss of energizer. Experiments with N_2–CO_2 mixtures passed through layers of charcoal with and without the admixture of energizers indicate that the latter act as catalysts for the reaction $CO_2 + C = 2CO$. In this way a high CO concentration is maintained near the surface of the steel and carburization is accelerated.—R. A. R.

Corrigendum

In the abstract of E. I. Malinkina's paper on increasing the ductility of high-speed steel (April *Journal*, p. 387), 'tempered' and 'tempering' should read 'annealed' and 'annealing' respectively.

Continuous Furnace for Fast Annealing of Tin-Plate. M. D. Stone and E. A. Randich. (*Metal Progress*, 1952, **61**, Feb., 62–66). A line in operation at the Gary sheet and tin mill of the United States Steel Co. incorporates all the items that must be considered in the successful processing of a high production, low-cost product. This line for finished tinplate and black plate can handle cold-rolled strip in thicknesses from 0·0075 to 0·015 in. and widths of 18 to 37 in. at a speed of 1000 ft./min. Its capacity is approximately 30 tons/hr.

The Theory of Hardening. P. Gomez Baeza and F. Muñoz del Corral. (*Inst. Hierro Acero*, 1951, **4**, Oct.–Dec., 323–337). [In Spanish]. A theoretical study is made of the reactions in the breakdown of austenite during isothermal transformation. Scheil's theory of 'interrupted quench' is applied to the drawing up of practical diagrams for the continuous cooling of austenite. The cooling curves used correspond to the properties of the centre portions of a series of round bars of infinite length in relation to diameter.—R. S.

Martempering: Invention and Early History. R. F. Harvey. (*Iron Steel*, 1952, **25**, Jan., 14–16). The author outlines the early history and development of the 'martempering' or 'step-quenching' method of heat-treatment, and discusses the advantages of the process.—G. F.

Fast Quench Oil Improves Hardenability in Aircraft Steels. J. McElgin. (*Iron Age*, 1952, **169**, Jan. 24, 72–74). Tests with a new quenching oil are described. This oil has been developed to meet the hardness requirements of aircraft steels.—A. M. F.

Are You Getting the Most from Your Water Sprays? W. P. Wallace and C. E. Manes, jun. (*Iron Age*, 1952, **169**, Jan. 31, 112–114). Experiments have been made to determine the heat-transfer rates between high-pressure sprays and heated steel. Cooling curves from 1480° F. for sprays at 10 and 90 lb./sq. in. are given, and the average convection coefficient is plotted against flow rate and pressure. From these it is shown that the convection coefficient may be expressed as $h_c = C(P \times Q)^n$ where C is a constant, P is the pressure, Q is the flow rate, and n is the slope of the line.—A. M. F.

Quench-Temper Treatment Improves Nodular Irons. J. E. Rehder. (*Iron Age*, 1952, **169**, Jan. 17, 89–93). The heat-treatment of nodular irons is discussed. These irons require at least 30 min. at 50° F. above the critical temperature range. Predominantly ferritic structures may require longer or soaking at higher temperature. Tempering at 1000° F. produced a tensile strength of 142,750 lb./sq. in. with 290 Brinell in a 3·10% carbon composition.—A. M. F.

FORGING, STAMPING, DRAWING, AND PRESSING

Methods of Forging. J. C. Stevens. (*Ing. e Indust.*, 1951, **19**, Oct., 106–108). [In Spanish]. The author discusses, in a general manner, the manufacture of rotors, crankshafts, and hollow forgings, and points out the importance of the direction of the grain flow.—R. S.

Die Forging of Steel. J. D. Latta. (West of Scotland Iron and Steel Inst.: *Brit. Steelmaker*, 1952, **18**, Feb., 82–88). The author describes in general terms the process of die forging and discusses the plant used. The principles of die design and the manufacture of dies are also considered, from both the production and the cost points of view.—G. F.

Structural Parts in High Pressure Plants for Producing Motor Fuels. A. F. Maier. (*Technische Mitteilungen Krupp*,

Technische Berichte, 1941, **9**, Dec., No. 5, 81–91). The production, especially by forging, of plant used the for manufacture of motor fuels is described. The materials used are first discussed, bearing in mind the different methods of producing motor fuel, their pressures, temperatures, and the likelihood of chemical attack. The forging of large seamless hollow vessels is described and illustrated. Diagrams are given for self-sealing lids and screw caps for pressure vessels, connections and flanged joints for high-pressure piping.—R. J. W.

The New Heavy Forge at Hadfields Ltd. (*J. Iron Steel Inst.*, 1952, **171**, Aug., 413–419. [This issue].

Stampings Formed Faster. H. Chase. (*Steel*, 1952, **130**, Feb. 4, 90–91). The production of two stampings are briefly described. One is a silo roof panel 17 sq. ft. in area, drawn from 0·070-in. steel, which is completely formed in one operation. The other is a tractor part formed from $\frac{3}{4}$-in. bar stock which had formerly to be forged.—A. M. F.

Stampings Make Strong, Accurate Camera Parts. H. Chase. (*Iron Age*, 1952, **169**, Jan. 10, 92–94). A short description is given of the production of stampings for camera parts. These include unusually small corner radii and depth for single operation stampings. Ribbed corners are made use of for stiffening purposes.—A. M. F.

Reduction in Cross Section, and Elongation, When Drawing Bars and Tubes. F. Rüberg. (*Metallwirtschaft*, 1943, **22**, Feb. 19, 107–110). Formulæ are first derived for the reduction in cross-sectional area of round bars and tubes from the commencement of drawing. Graphs are drawn of the diameters and cross-sections for different percentage reductions. Numerous examples are given describing the most advantageous manner of using this information. A formula is then developed in which the elongation is shown as a percentage of the cross-sectional area.—R. J. W.

The Testing of Deep Drawing Materials by the 'Tensile Wedge' Drawing Process. H. Kayseler and W. Püngel. (*Mitteilungen der Kohle- und Eisenforschung*, 1939, **2**, Nov., 4, 141–155). The usual deep-drawing experiments on sheet metal do not yield a sufficiently close estimation of the practical deep-drawing properties of sheets for multiple drawing. In the series of experiments described, the deep-drawing properties of previously prepared specimens were examined, these specimens having had different amounts of cold working. The 'tensile wedge' method of testing is described. The manner in which the accepted value of the ductility is altered by the deep-drawing stresses is followed by this method.

Plant and Equipment for Working and Drawing Wire. A. Frascio. (*Riv. Mecc.*, 1951, **2**, Oct. 13, 5–10; Oct. 27, 15–19). [In Italian]. The author describes the principles to be followed in modern wire-drawing plant. Layout diagrams are given together with descriptions of handling appliances, wire-drawing machinery, and pickling plant.—M. D. J. B.

The Effect of Tempering on the Elastic Properties of Steel Wire. W. Püngel and R. Hünlich. (*Mitteilungen der Kohle- und Eisenforschung*, 1940, **2**, Mar., 185–188). In hard-drawn steel wire, the 0·01 and 0·03 proof stresses will increase by tempering at 200–300° C. to a value double that of the initial state. By attaining such high values at one tempering temperature, the fatigue limit is decreased as such low temperatures necessitate long tempering times. The effect of tempering is the same on both the 0·2 proof stress and the fatigue strength of the wire. The residual extension is already increased by changing the tempering temperature from 100° to 200° C. and rises further with increasing the tempering temperature and time.—R. J. W.

The Effect of Pre-Annealing Rolled Wire, the Patenting Temperature and the Surface Decarburization on the Properties of Steel Wire. W. E. Wagenknecht. (*Mitteilungen der Kohle- und Eisenforchung*, 1940, **2**, Mar., 5, 159–184). In the manufacture of wire for ropes a pre-anneal of the rolled wire at 700° C. gave a small improvement in nearly all the properties tested. A decarburizing recrystallization at 1000° C. produced a small reduction in the tensile strength, but a considerable improvement in the properties of the wire in the bending and twisting tests. Surface decarburization lowers the true alternating fatigue limit with alternating repetition of stress although in certain cases it is often advantageous. Free ferrite in patented wire influences all the properties of the finished wire in a very unfavourable manner and should always be avoided.—R. J. W.

Calculation of Drawing Die Dimensions for Multiple-Draw Machines. W. Lueg. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 95–101). The procedure given by E. L. Baay, for the graphical determination of intermediate die diameters for wire drawing on a multiple-draw machine with equal or varying reductions at each pass, is described and developed. By introducing auxiliary scales, a further group of reference lines and a second nomogram field, a general diagram has been devised with which die diameters and all other characteristics may be rapidly and reliably determined for drawing processes with any type of sequence. The use of an ordinary slide rule for solving the same problems is fully described. The die diameter, individual and total reductions, increase of length and number of draws can be determined with a few movements only of the slide rule. Finally, relationships are derived from which to calculate the minimum reduction of a multiple-draw machine in which the speeds of the individual sheaves are fixed. It is shown that the smallest reduction of cross-section of such a machine is determined only by the ratio of the speeds of the first and last drawing stages.—J. P.

The Working of Metals: Deformation during Wire Drawing and Rolling. W. C. F. Hessenberg. (Institute of Metals: *Iron Coal Trades Rev.*, 1952, **164**, Jan. 18, 135–140; *Metal Ind.*, 1952, **80**, Jan. 11, 50–52; Jan. 18, 50–53). The author discusses the distribution of energy in metal-working processes with special reference to wire-drawing and rolling-mill operations. The use of plasticine models to compare and study the flow under deformation is described, and the subject of friction during rolling is also considered.—G. F.

ROLLING-MILL PRACTICE

Modern Controls and Drives for Rolling Mills. C. v. Kissling. (*Stahl u. Eisen*, 1952, **72**, Feb. 14, 165–174). The development of control gear for rolling-mill drives, particularly in the U.S.A., is reviewed. The requirements of amplifying equipment and the application of individual types are discussed; those for strip mills necessitate exact control of each roll, of the relative speeds of the rolls in the train, and of strip tension. Twin drives for strip mills and their control mechanism are described. The application of amplifiers has made the control of reversing blooming mills more efficient and has made it possible to apply current limitation so as not to overload the mill equipment.—J. P.

Measurement of Drawing Force, Roll Force and Rolling Power with Electric Resistance Strain Gauges. K. Fink and W. Lueg. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 151–156). A simple arrangement of resistance strain gauges and a Stabe continuous recorder has been developed for measuring drawing force, roll force, and rolling power; this will record two variables simultaneously and requires no amplification of the output from the gauges and no wet development of the records. The suitability of the arrangement for operational use has been demonstrated by measurements of (*a*) drawing force in bar drawing at different speeds, and (*b*) roll force and roll torque in the cold rolling of strip steel under various rolling conditions.—J. P.

Time Study of Rolling-Mill Operations. C. Murski. (*Hutnik* (Katowice), 1952, **18**, Feb., 42–47). [In Polish]. Time of rolling as a function of output and the planning of work in rolling mills are discussed.—V. G.

The 'Pressure Weldability' of Mild Steel Under the Pressure of Rolls. R. Walzel and H. Lipold. (*Berg- hüttenmänn. Monatsh.*, 1941, **89**, Nov., 129–137; Dec., 143–147). Using small experimental rolls, with mild-steel strip, (15 × 1 mm. cross-section), the pressure weldability was measured after rolling under a range of different conditions after different heat-treatments. Steels of various compositions were used, particular attention being paid to the silicon, phosphorus, and copper contents. With annealing in an oxidizing atmosphere before rolling, increasing the silicon content reduced the pressure weldability considerably whilst this effect was not so marked after a prerolling anneal in a reducing atmosphere. The effect of phosphorus and copper was not so great. The strength of the welds increased with greater rolling pressure and annealing temperatures.—R. J. W.

Device for Hot Rolling Sharp-Angled Tees. L. Gascuel. (*Mét. Constr. Méc.*, 1951, **83**, Dec., 991–995). Following a brief note on the calculation of spread and the effect of temperature on rolling, the roughing and finishing passes for tees are described. A 'superfinishing device' which lessens imperfections in the section is considered. It consists of two

Ni–Cr steel rollers at right angles mounted on the lower part of the stand. Two methods are used to control the roll pressure on the inner corners of the tees: (1) A device controlled by a square thread screw moving both rollers longitudinally; and (2) a modification of the first device where one roller moves longitudinally to operate on the thickness of the tee and the other, vertically, operates on the flange.—R. S.

The Rolling-Mill Stands at Fried. Krupp Grusonwerk Aktiengesellschaft, Magdeburg-Buckau. (*Technische Mitteilungen Krupp, Technische Berichte*, 1941, **9**, Dec., No. 5, 95–104). An historical review is given of the development of the rolling-mill stands at the Krupp Grusonwerk from the building of the first simple 2-high rolling machine in 1833 to the large works in 1941. A wide variety of hot and cold rolling mills for ferrous and non-ferrous metals has been developed to a high degree of technical perfection. The improvement and perfection of sheet and strip mills is followed, and mention is made of the subsidiary equipment developed.—R. J. W.

Control of Gauge Variations with Speed Changes in Cold Strip Rolling. (*Brit. Steelmaker*, 1952, **18**, Feb., 80–81). This article summarizes experiments on the effect of speed changes in cold strip rolling on the strip gauge, and mentions the B.I.S.R.A. system of automatic closed-loop gauge controls for preventing the speed effect.—G. F.

Roll Size Effects in Rolling of Strip. N. H. Polakowski. (*Metal Progress*, 1952, **61**, Feb., 67–71). The author explains why roll diameter limits the maximum draft and minimum thickness but has no important effect on the power required per ton of thin strip rolled.—J. P. S.

The Use of Coil Furnaces in Wide Strip Rolling Mills. H. P. Lemm. (*Technische Mitteilungen Krupp, Technische Berichte*, 1940, **8**, Dec., No. 5, 89–96). The use of box-type furnaces around specially designed coiling reels in both continuous and semi-continuous wide strip rolling mills is discussed. The positions of these furnaces in the rolling-mill train are clearly shown in diagrams and photographs for both Steckel and Röchling rolling mills. The first installation of this type in Europe was at the Krupp-Gruson works where initial expectations were fully realized.—R. J. W.

Ingot Tippers in the Rolling Mill. H. P. Lemm. (*Technische Mitteilungen Krupp, Technische Berichte*, 1942, **10**, Nov., No. 3, 55–65). Many sectional diagrams and photographs are given of manipulators for displacing and tipping ingots of various sizes in a rolling mill, together with sketches of their mode of operation. Forked edge tippers which tip the billet through 45° or 90°, stationary twisting guides, and tipping roll tables with different amounts of guidance and flexibility are included, together with billet tippers for grooved rolls and rotary tippers to tip through 90°. Finally tongs, between which the ingot is grasped and then turned on its side, are described, the mechanism for which may be above or below ground.—R. J. W.

Roller Tables with Individual Drives. T. Sluszkiewicz. (*Hutnik* (Katowice), 1951, **18**, Dec., 491–494). Various types of roller table and factors of importance in the design of the drive transmission are discussed.—V. G.

WELDING AND FLAME-CUTTING

New Method for Thermit Welding of Rail Joints in Tram Tracks. V. V. Lapshin and M. I. Login. (*Avtog. Delo*, 1949, No. 7, 19–20). [In Russian]. Various modifications of thermit welding are discussed, and one specially suitable for tram tracks is described. In this new technique, no special end-preparation is necessary and the working surfaces of the rails are protected.—S. K.

Spot-Welding of SKhL-2 Steel with Electric Heat-Treatment. A. S. Gel'man and S. S. Astaf'ev. (*Avtog. Delo*, 1949, No. 11, 7–14). [In Russian]. Experiments are described on the properties of spot welds produced with subsequent electrical heat-treatment. Specimen pairs of plates of the same thickness, 4, 5, and 7 mm. thick, were used of low-alloy steels (Cr 0·4–0·8%, Ni 0·3–0·7%, Cu 0·3–0·5%). Temperatures at the specimen–electrode contact surface were measured by thermocouples built into the electrode, and the time–temperature curve for optimum conditions is given. Tensile tests and hardness traverses extending 1 cm. on either side of the spot welds were made. On the basis of these tests the minimum length of time between the end of welding and the start of the heat-treatment *in situ* was determined. Macro- and microstructures of the spot and base metals are reproduced to show that, as a result of the electrical heat-treatment, tempering and partial recrystallization take place, accounting for the improved properties. The effect of electrical heat-treatment increases with decreasing specimen thickness and increasing hardenability. The advantages of the process are: (1) High plastic properties of the joints obtained make the process suitable for structures of alloy steels hardenable under the conditions of rapid cooling in the spot zone; (2) small deformations on welding, due to the short duration of the heat-treatment; and (3) moderate current consumption. The disadvantages are the necessity for more powerful equipment and the greater duration of the welding cycle. The process is recommended for low-alloy structural steels and for pearlitic alloy steels, *e.g.*, Chromansil.—S. K.

Welded Tangential Cutters. A. V. Sobolev and N. E. Budnikov. (*Avtog. Delo*, 1949, No. 7, 24–26). [In Russian]. The effect of pressure during the flash-welding of high-speed and other steels to form cutter blanks, and the effect of their subsequent heat-treatment on the properties of the joint are described.—S. K.

Control of Welded Tubes by Gamma-Ray Irradiation. S. M. Skorodzievskii. (*Avtog. Delo*, 1949, No. 7, 27). [In Russian]. Two methods of using gamma-rays for testing the quality of welds in pipelines are described, as well as a device assisting the interpretation of the figures obtained. A nomogram for estimating exposures is given.—S. K.

The Thermal Control of Spot Welding. K. A. Kochergin. (*Avtog. Delo*, 1949, No. 9, 9–10). [In Russian]. The temperature distribution in and near each joint in spot welding is considered. The results are presented of measurements of the temperature under the electrode corresponding to various current strengths, electrode pressures, and welding times, and the strength of the spot welds in 4-mm. sheets is given.—S. K.

Investigation of the Strength of Welded Structures Working under Impact. G. I. Pogodin-Alekseev. (*Avtog. Delo*, 1949, No. 7, 4–8). [In Russian]. An account is given of a laboratory investigation on the effect of the thickness of structural steel plates and their arrangement on the impact strength of single and multiple-plate specimens. Specimens were prepared from steel plates (C 0·38%, Mn 0·67%), 2·5, 5, or 7·5 mm. thick, their breaking energies being found for loose and welded plates. Impact tests were also carried out on smooth and drilled specimens of very low carbon steel plates (C 0·04%) deposited by arc welding. In general, the impact strength of composite specimens was greater than that of single-plate specimens only if the plates were securely welded along their edges.—S. K.

The Real Safety Factor of Welded Joints. Ya. M. Libktarnikov. (*Avtog. Delo*, 1949, No. 7, 8–10). [In Russian]. The results are given of mechanical tests on 1040 specimens made from butt-welded plates of steels with the following respective compositions: Carbon, 0·18 and 0·14%; manganese, 0·44 and 0·40%; silicon, traces; sulphur, 0·025 and 0·016%; phosphorus, 0·015 and 0·024%. The welding was carried out automatically and manually with high-quality Russian and foreign coated electrodes, and tensile and bending tests were made. The frequency curves for these properties for specimens welded by the different electrodes are presented, and the maximum and mean safety factors are calculated by comparison with standard values.—S. K.

Automatic Welding of Reservoirs at Low Temperatures. A. S. Fal'kevich and V. S. Volodin. (*Avtog. Delo*, 1949, No. 7, 21–24). [In Russian]. An account is given of an investigation of the effects of welding low-carbon steel at temperatures from 0° down to −20° C. on the properties of butt- and lap-welded joints produced by the automatic submerged-arc welding.—S. K.

The Mechanism of the Crystallization of Weld Metal During Fusion Welding. A. A. Alov. (*Avtog. Delo*, 1949, No. 9, 1–3). [In Russian]. The forces acting on the fused metal as it crystallizes in arc welding with bare and thickly coated electrodes, and in submerged arc welding, are considered. It is concluded that, under the action of these mechanical forces, the metal is periodically displaced from the molten pool in the form of waves, flowing up to the more or less solidified metal of the previous waves. The traces left by the wave-like movement and crystallization on the outer surface and inner structure of the seam are described, and the nature and frequency of the waves are considerably influenced by the welding conditions and the properties of the electrode coatings and fluxes.—S. K.

Cutting and Flame Processing. R. S. Babcock. (Amer. Welding Soc.: *Blast Furn. Steel Plant*, 1952, **40,** Feb., 215–219). The author reviews the recent developments in cutting and flame processing—cutting up heavy scrap, recovery, steel conditioning, powder injection processes, and piercing holes in rock formations by a stream of hot gas at high velocity from a chamber in which kerosene and oxygen are burned.

Dependence of the Oxygen-Cutting Speed on the Design of the Oxygen Nozzle. L. A. Peletier and C. F. Belderbos. (*Schweissen u. Schneiden*, 1952, **4,** Mar., 79–80). An investigation on the influence of the size of the oxygen-gas jet on cutting speed is reported. When cutting 1-in. plate with oxygen at 60 lb./sq. in. the maximum cutting speed was obtained with a jet 1 mm. in dia. the exit end of which was 1·2 mm. in dia. for a length of 6 mm.—R. A. R.

Heavy Scrap Cutting in the Steel Mill. L. P. Elly. (*Welding J.*, 1952, **31,** Feb., 97–101). Oxygen/fuel-gas cutting of heavy melting scrap for open-hearth furnaces is described. Considerable time was saved and in 18 months' operations, an average of 8·69 short tons of scrap were prepared per machine per man hour, consuming an average of 625 cu. ft. of oxygen and 34 cu. ft. of fuel gas per short ton of prepared scrap.—U. E.

CLEANING AND PICKLING

The Action of Inhibitors in Pickling. A. Indelli and G. P. Bolognesi. (*Met. Ital.*, 1952, **44,** Feb., 73–77). After considering pickling inhibitors in general the authors discuss the action of allyl isothiocyanate and give data on the volume of hydrogen evolved at two different temperatures in pickling tests. The mechanism of the action of the allyl isothiocyanate in relation to the acid concentration is then examined by an electrochemical method. Lastly, the authors describe tests to determine the efficiency of the pickling inhibitor having regard to costs and the corrosion resistance of the surfaces obtained. (33 references).—M. D. J. B.

Pickling and Pickling Acid Inhibitors. A. Douty. (*Metal Ind.*, 1952, **80,** Feb. 8, 108–110). Several of the more important classes of organic inhibiting compound are listed, and the mechanism and measurement of inhibition are described. An adsorbed film is formed on the metal surface and its effectiveness may be measured by change in electrical resistance. The phenomena of hydrogen absorption and embrittlement are dealt with. (15 references).—P. M. C.

Descaling of Carbon Steels in Modern Merchant Mill Practice. C. S. Lambert. (*Iron Steel Eng.*, 1952, **29,** Feb., 59–63). After considering the problems of producing bars free from rolled-in scale, and tearing, shearing, and other superficial defects, the author discusses primary and secondary scale, *i.e.*, that which is formed on the billet in the reheating surface and that formed during the rolling process. Methods of removing scale are dealt with. The best way is to use high-pressure water. This process, in addition to producing scale-free bars, substantially increases roll life, reduces delays due to changing or grinding guides, and reduces guide shearing and tearing.—M. D. J. B.

Regeneration of Sulphuric Acid in Waste Pickle Liquors. E. W. Mulcahy. (*Inst. Chem.*, 1952, **28,** Mar., 125–129). In the steel industry, regeneration is performed by cooling and precipitating the ferrous salts. This is either carried out in batches, or, more recently, continuously. The continuous regeneration system is described with the aid of a flow diagram, and it features a heat exchanger in which regenerated acid passes in counter current to the hot waste acid, thus appreciably conserving heat. Copperas crystals are now marketable. Electrodeposition is used for recovery in the copper industry.—T. E. D.

The Cleaning of Metals in Engineering Processes. I. B. McKenzie.. (Australian Inst. Metals: *Australasian Eng.*, 1951, Dec. 7, 87–93, 137–141). The following mechanical cleaning methods are first described: Tumbling and rolling; blasting; wire brushing; flame cleaning; and furnace treatment. Chemical methods are next dealt with: Pickling, alkaline cleaning, and salt-bath descaling being described. Finally, solvent cleaning is discussed with particular reference to petroleum distillate washing, vapour degreasing, and emulsifiable and diphase cleaners. (33 references).—P. M. C.

Barrel Finishing. (*Metal Ind.*, 1952, **80,** Feb. 8, 105–100). Details are given of a new type of barrel finishing or rumbling machine developed by the Fox Chemical-Engineering Works, Ltd., London. The unique feature of this 'Polymotion' machine is that the barrel is offset through the axis of rotation. Excellent work is produced, and research work is being carried out on synthetic barrelling media for both dry and wet use.

Laboratory Tests Select Best Blast-Cleaning Method. E. F. Anderson. (*Steel*, 1952, **130,** Jan. 21, 62–65). Selection of the best airless blast-cleaning method for a given application can be determined most effectively by laboratory tests. At a demonstration in a laboratory a customer's work is cleaned by the type of equipment he proposes to use in actual production. The laboratory is equipped with standard and special cleaning units. The special cabinets are adjustable so that engineers can try many combinations and positions of abrasive throwing units and different conveyor speeds.—A. M. F.

Jobbing Shotblast: Over Half a Century of Development. (*Iron Steel*, 1952, **25,** Jan., 17–19). A brief description is given of the history and development of R. J. Richardson and Sons, Ltd., one of the leading firms in the shotblasting industry, and the present-day layout of the plant and the type of work undertaken are discussed.—G. F.

PROTECTIVE COATINGS

Plating High-Tensile Steels. H. Cann and V. F. Henley. (*Aircraft Prod.*, 1952, **14,** Mar., 87–88). Methods of mechanical and chemical pretreatment are surveyed. Selective plating is mentioned, and also the deposition of nickel, chromium, brass, cadmium, and zinc. Heat-treatment after plating is often necessary.—T. E. D.

Plating Hints. T. M. Rodgers. (*Metal Ind.*, 1952, **80,** Feb. 22, 147, 148). The article is confined to a discussion of correct maintenance of electrical installations. The care of rectifiers, ammeters, and busbars is dealt with, and the various undesirable effects of stray currents and the need for good insulation are discussed.—P. M. C.

Metal Fabrication by Electroforming. A. Whittaker. (*Machinery*, 1952, **80,** Feb. 7, 240–242). The article reviews the development of the electroforming process (production of metal components by depositing metal electrolytically on master formers, which may be parted, after plating, from the deposited shell) and outlines the stages involved, so that production engineers may appreciate its possibilities.—E. C. S.

Thickness Measurement of Deposited Coatings. B. Bianchi. (*Riv. Mecc.*, 1951, **2,** Sept. 15, 15–19). [In Italian]. The method for determining the thickness of deposited coatings comprises bringing a small emery wheel in contact with the surface to be measured. A small area of the coating is then ground away down to the base metal at a very flat angle giving a projected thickness easily measured with a portable microscope. The actual thickness is then rapidly obtained from a nomogram.—M. D. J. B.

Study on the Method to Measure the Thickness of Non-magnetic Layer on Steel (I). O. Ito. (*J. Mech. Lab.*, 1951, **5,** Aug., 153–156). [In Japanese]. The method consists of measuring the force required to separate a magnet from the coated steel article by a self-compensating magnetic balance.

The Role of Electroplating in Engineering. S. M. Anderson and H. E. Arblaster. (*Australasian Plating Fin.*, 1951, **1,** Sept., 4–9, Oct., 4–10). The following applications of electroplating are briefly discussed and some examples described: (1) Corrosion prevention; (2) assistance to other processes, *e.g.*, deposition of nickel to secure better adhesion of enamel, and 'stopping off' in hardening processes; (3) wear prevention; (4) building up worn parts; and (5) fabrication by electroforming.—R. A. R.

Current and Metal Distribution in Electrodeposition. II. Theoretical Considerations. J. Kronsbein. (*Plating*, 1952, **39,** Feb., 165–170). Some simple fundamentals concerned with primary current distribution are given, with a minimum of mathematical treatment. Known cases of uniform current and metal distribution are discussed and formulæ are derived for calculating current distribution on inside and outside corners.—J. P.

Clad Steel Bullet Jackets Conserve Copper and Zinc. E. J. Reardon. (*Steel*, 1952, **130,** Jan. 21, 68–69). A new method of cladding steel with gilding metal is producing billets weighing 2000 to 3000 lb., up to about 17 in. wide, and raising the yield of usable clad strip. A steel plate can be clad with different alloys on each side.—A. M. F.

Interpretation of Specifications for Electroplated Coatings. S. Wernick. (*J. Electrodep. Tech. Soc.*, 1950, **26,** 221–235). The author describes the principal difficulties encountered

when drawing up specifications which are practical and fair to both the customer and plater. Revision of British Standard 1224, which specifies 0·0008 in. of nickel and was intended for nickel plus chromium coatings, is imperative if regard abroad for British finishes is to be maintained. It is urged that specifications in performance be adopted, and that manufacturers should agree on what constitutes a fair test.

Questions of Hygiene in Surface Treatment of Metals. W. Schmid. (*Metalloberfläche*, 1951, **5**, Feb., B24–B26). Hazards to health involved in metal cleaning, spraying, galvanizing, and enamelling are discussed and methods for adequate protection are indicated.—P. F.

Hard Chromium Coating—Its Properties and Uses. J. Agullo Marly and J. B. Vericat Raga. (*Ing. e Indust.*, 1951, **19**, Oct., 77–84). [In Spanish]. The author endeavours to define mathematically the life of a chromium coating in terms of hardness, temperature, surface finish, working pressure on the surface, lubricating effect, resistance to corrosive media, and effect of abrasives and other factors such as composition, porosity, passivity, and magnetization. Wear-resisting applications are discussed under the headings: Dry friction; lubricated friction; and friction in the presence of abrasives. A brief comparison is made of chromium coatings and case-hardened surfaces as regards wear resistance.—R. S.

Recovery of Chromic Acid from Plating Operations. F. R. Keller, C. C. Cupps, and R. E. Shaw. (*Plating*, 1952, **39**, Feb., 152–154). Marked savings of chromic acid have been effected at the standard Steel Spring Co.'s works at Newton Falls, Ohio, by paying special attention to the amount of drag-in to, and drag-out from, the plating tanks. The rinsing water from the first rinse tank is concentrated and run back to the plating tank.—J. P.

Chromic Acid Anodizing Equipment and Its Practical Use. H. E. Head. (*Plating*, 1952, **39**, Jan., 40, 41, 50). The installation and operating methods at the Briggs Manufacturing Co., Detroit, are described.—J. P.

Metal Economy through Chromizing. H. Kalpers. (*Metall*, 1951, **5**, Dec., 546–548). The author shows by examples what scope there is for the saving of corrosion and scale-resistant alloys by impregnating the surface of low-carbon steels with chromium. Among the examples quoted are silencer pipes for internal combustion engines, condenser tubes, and exhaust valves.—J. G. W.

The Protection of Metallic Surfaces by Chromium Diffusion. R. L. Samuel and N. A. Lockington. (*Metal Treatment and Drop Forg.*, 1951, **18**, Aug., 354–359; Sept., 407–415; Oct., 440–444; Nov., 495–502, 506; Dec., 543–548, 556; 1952, **19**, Jan., 27–32; Feb., 81–85). Part I is an historical survey of the development of earlier chromizing processes. In the second part, theoretical aspects of all processes by which one metal is coated with another by chemical deposition from the gas phase at high temperatures are considered, with particular reference to iron and steel. Thickness and composition of chromized coatings, and the influence of temperature, time, and gas pressure are discussed. Part 3 gives particulars of the structure of chromized coatings. The effect of temperature on the grain size of coat and core, and the effect of carbon and other alloying elements on the final structure are described. Chromizing methods which have been developed since 1938 are discussed in Part 4. Of these the German B.D.S., and the British D.A.L. processes, both of which employ pack-chromizing techniques, are the most practicable and are in commercial use. The future development of the salt-bath method for small parts is also discussed. In Part 5, hardness, ductility, and weldability of coatings are dealt with, and original data on the resistance to corrosion and oxidation in various media are given. The efficiency of method and equipment receives attention in Part 6, and many examples of the application of chromizing to impart corrosion and heat resistance are described. A combined Cr–Si–Al diffusion treatment, which produces a coating resistant to temperatures in the region of 1050° C. is also described. The improvement of the wear and abrasion resistance of drop-forging dies and other tools is dealt with in Part 7. (50 references).—P. M. C.

Thermal Dependence of Elastic Constants of Electrodeposited Chromium. H. Pursey. (*Nature*, 1952, **169**, Jan. 26, 150). The variation of Young's modulus and the modulus of rigidity in the temperature range 10–80° C. has been studied at frequencies varying from 15 to 160 kilocycles/sec.—A. G.

Testing Methods for Galvanic Nickel Baths and Coatings. J. Elze. (*Metall*, 1952, **6**, Jan., 5–11). Tests of adhesion, porosity, hardness, suitability for chromium plating, residual stresses and so on, with regard to nickel coatings, and tests of both activity and exhaustion, are briefly discussed, using information from the literature and the author's experimental data.—J. G. W.

Substitutes for Nickel in Electroplating. J. J. Dale. (*Plating Notes*, 1951, 3, Oct., 163–173). The properties and merits of chromium, copper, and zinc coatings are compared with a view to giving guidance on which to select as a substitute for nickel.—R. A. R.

Tin Plating Advances Save Metal. (*Steel*, 1952, **130**, Jan. 21, 66–67). New methods for determining tinplate coating weights, data on tin–zinc plating bath composition and effect of variables on the tin–nickel alloys composition are reported. The coating-weight method is based on the fact that anodic dissolution of tin coatings on steel proceeds with full current efficiency in hydrochloric acid enabling the weight of a defined area to be calculated from Faraday's law.—A. M. F.

Hot-Tinning of Cast Iron. (*Metalloberfläche*, 1951, **3**, Feb., B19–B21). This is a review of the literature relating to German, American, and British methods of hot-tinning cast iron.—P. F.

Lead–Tin Alloy Plating for Solderability. J. W. Cuthbertson. (*J. Electrodep. Tech. Soc.*, 1950, **26**, 99–106). The main factors concerning the solderability of electrodeposited tin coatings, *viz.*, thickness, ageing, and nature of basis metal are first discussed. It is possible that, owing to the slower rate of diffusion of copper in lead alloys at room temperature, lead–tin coatings deteriorate in solderability more slowly with age than do pure tin coatings. The constitution of and working conditions for known baths for plating lead–tin alloys are reviewed.—R. L. B.

Development of Methods of Drying Steel Sheet. A. Merz. (*Metalloberfläche*, 1951, **5**, Apr., A57–A60). The historical development over the last 50 years of plant and methods of drying lacquer and other coats on steel plates is traced. The design of recent plant is discussed and the merits of infra-red drying are considered.—P. F.

PROPERTIES AND TESTS

The Properties of Metals and the Periodic System. H. Sieglerschmidt. (*Metall u. Erz*, 1943, **40**, Aug., 222–228). A very clear and simple presentation of the relationship between certain properties of matter and their position in the periodic table is given. Rules are given relating the specific gravity, the valency, the melting point, and the coefficient of expansion to the atomic number.—R. J. W.

Contribution to the Problem of the Relationship Between the Grain Size and the Properties of Steel. A. Legat. (*Berghüttenmänn. Monatsh.*, 1940, **88**, Mar., 29–35). The properties of steels are very dependent on the grain size, this size indicating the degree of nucleation. If a fine-grained steel is subjected to a nuclei-dissolving heat-treatment which does not increase the grain size, the steel will possess properties characteristic of a coarse-grained steel, in spite of the fine grain size of the austenite. The critical cooling velocity depends predominantly on the capacity for sub-cooling. The hardenability and capacity for self-annealing, and their dependence on the state of nucleation of the steel, were investigated.—R. J. W.

The Influence of Impurities on the Properties of Metals. J. D. Fast. (*Metalen*, 1952, **7**, Jan. 15, 2–12; Jan. 31, 23–27; Feb. 15, 48–50). [In Dutch]. Pure metals and impurities are defined. The latter are discussed under soluble and insoluble varieties. The following factors are considered: Oxygen and sulphur in iron; inclusions and the inhibition of crystal growth; precipitation of inclusions from a supersaturated solid solution; and the subsequent hardening and increase in creep strength. The effects of carbon and nitrogen in pure iron and in iron containing 0·5% Mn explain magnetic ageing. Interactions between impurities and dislocations are examined. Cottrell's theory explains some, but not all, of the facts in connection with strain ageing.—R. S.

Contribution to the Knowledge of the Effect of Velocity in the Hot Tensile Testing of Steels. H. von Laizner and R. Walzel. (*Berg- hüttenmänn. Monatsh.*, 1943, **91**, Mar., 27–41). The tensile properties of three steels (with 0·10%, 0·24% and 0·45% C respectively) were measured in the temperature range 20° to 700° C. at 100° intervals. Two rates of loading were used at each temperature; in the 'slow' experiments

about 5–10 min. elapsed before fracture occurred, whilst the 'rapid' experiments took only 3–10 sec. A record of the stress/strain diagram was taken for the latter. Results are given diagramatically and in tabular form for the tensile strength, breaking stress, percentage reduction in areas and elongations for the various temperatures.—R. J. W.

Study for Applying Material (X). On the Criterion of the Test of the Notched Specimen of Steel Plate. H. Matsumoto and K. Kimura. (*J. Mech. Laboratory, Japan*, 1951, **5,** Dec., No. 8, 321–330). [In Japanese]. With regard to the tensile testing of notched steel plates, the authors find the maximum shear stress theory satisfactory for thick plates and consider it more sensitive than the ordinary tensile test.—J. G. W.

Device for the Investigation of True Stresses. L. Gillemot. (*Acta Technica Academiae Scientiarum Hungaricae*, 1951, **1,** 3, 191–197). [In German]. A device is described which facilitates the automatic recording of true stresses up to the point where necking occurs. As the device can be attached to any pendulum-controlled tensile-testing machine, true stresses can be recorded directly instead of, or in addition to, the stresses referred to the initial cross-section.—P. F.

Plastic-Wave Propagation Effects in High-Speed Testing. E. H. Lee and H. Wolf. (*J. Appl. Mech.*, 1951, **18,** Dec., 379-386). A material test carried out at high speed may be markedly influenced by plastic wave propagation effects. In such a case a variation of strain occurs along the test specimen and the stress/strain relation cannot be determined from measurements made on the specimen as a whole. If average values are taken, it is shown that a spurious strain-rate influence will be deduced when propagation effects first begin to appear as the testing speed is increased. The effect is not due to a true material strain-rate dependence, but to the appearance of strain variations along the specimen, and its magnitude depends upon the dynamics of the whole test arrangement. The theoretical plastic-wave analysis of a particular test arrangement is also given. The range of speed is determined which permits satisfactory interpretation without the need for detailed analysis of plastic-wave propagation.—J. P. S.

The Micro-Bend Testing Machine. K. Futaki. (*J. Mech. Lab.*, 1951, **5,** Sept., 221–224). [In Japanese]. A bend tester suitable for testing spinning needles is described.

How Accurate Is the Impact Test? Metallurgical and Research Committee of the Forging Manufacturers' Assoc. (*Metal Progress*, 1951, **60,** Dec., 69–71, 176). Sufficient heat-treated bar stock was supplied to several co-operating laboratories. The bars were machined from $\frac{5}{8}$-in. hot-rolled quenched and tempered steel. The survey included Izod- and Charpy-type machines. The data so far collected indicate that there is serious deviation in the results from most individual machines. Even greater inconsistences were found among the average results for each of the machines. The reproducibility of impact test results decreases as the impact resistance decreases when using the standard machines.

On the Mechanism of Cold Brittleness in Metals. T. Sutoki. (*Sci. Rep. Res. Inst. Tôkohu Univ.*, A, 1949, **1,** May, 23–28). [In English]. Charpy tests with various forms of the notch, and tensile tests at various straining speeds, were carried out on Flodin iron, 0·3 and 0·7% carbon steels, zinc, and aluminium, at temperatures ranging from that of liquid nitrogen to 200° C. The transition from ductile to brittle fracture is greatly influenced by experimental conditions. The author suggests that the fracture is brittle when it occurs within less than the time needed by a dislocation to move one atomic distance.—J. G. W.

Determination of Residual Stresses in Case-Hardened Parts. Part 3—Determination of Stresses in the Interior of Case-Hardened Parts. Part 4—Applications and Conclusions. J. Pomey, F. Goutel, and L. Abel. (*Métaux-Corrosion-Indust.*, 1951, **26,** Oct., 377–391). Metallographic methods for determining stresses are considered and the need for improvement is discussed. A new method, based on hardness measurements, is developed mathematically and the experimental technique is explained.—B. G. B.

Summarized Proceedings of a Conference on Stress Analysis, Liverpool, 1951. E. K. Frankl. (*Brit. J. Appl Phys.*, 1952, **3,** Apr., 105–114). The fifth annual conference of the Stress Analysis Group of the Institute of Physics was held in April, 1951. Nine papers dealing with statistical methods, electric resistance strain gauges, developments in France, fatigue, and photoelastic work were read and are here summarized.

Experimental Stress Analysis. N. Gross. (*J. and Trans. Soc. of Engineers*, 1951, **42,** Apr.–June, 63–88). Investigations of strain in pressure vessels and structures by means of models, analogues, photoelastic methods, brittle coatings, and strain gauges are surveyed. Optical, mechanical, and electrical strain gauges are mentioned in some detail, and an account is given of the study of a full-scale boiler drum under pressure, by means of electric resistance strain gauges. Examples of stress patterns in pipe bends are shown. (31 references).—T. E. D.

Theories of Deformation of Polycrystalline Materials. P. Laurent. (*Métaux-Corrosion-Indust.*, 1951, **26,** Nov., 433–441). Examples of several proposed theories are given and discussed, including those of Taylor and of Kochendörfer. Though great advances have been made in the study of polycrystalline materials they are less advanced than those for single crystals. The theory of consolidation of stresses is considered to be a useful advance.—B. G. B.

The Lüders Deformation of Mild Steel. E. O. Hall. (*Proc. Phys. Soc.*, 1951, **64B,** Dec. 1, 1085–1086). Photographs of thin strip specimens of mild steel plastically deformed at room temperature and at 200° C. are presented. The specimen deformed at room temperature appears straight when removed from the testing machine, whereas the one deformed at 200° C. has a distinct curvature in the plane of the wide front face of the strip. The author suggests that there may be a correlation between this phenomenon and the form of the Lüders bands obtained in the test pieces.—C. J. B. F.

Electrical Resistance Strain Gauges. G. Moravia. (*Riv. Mecc.*, 1951, **2,** Oct. 13, 15–17). [In Italian]. A brief description is given of the electrical resistance strain gauge, its mode of operation and its numerous applications in modern engineering science.—M. D. J. B.

Practical Stress Analysis with Electric Resistance Strain Gauges. O. Krisement. (*Arch. Eisenhüttenwesen*, 1952, **23,** Mar.–Apr., 157–161). The formulæ required for stress measurement of a homogeneous and isotropic specimen stressed within its elastic limit are derived. Some of the many processes and the equipment for rapid assessment are described. There follows a discussion of the types of strain gauge rosette that are mainly employed, and of the transverse sensitivity of strain gauges.—J. P.

Measurement of Residual Stresses in Bars and Tubes by Means of Strain Gauges. H. Bühler and W. Schreiber. (*Z.V.d.I.*, 1952, **94,** Mar. 11, 216–218). The article deals with practical difficulties arising from the use of electrical resistance strain gauges. The authors recommend vacuum drying instead of the usual drying by heat, so as to avoid changes in residual stresses, and a circuit which averages automatically the stresses over the circumference of the part. An example of the use of the method is given.—J. G. W.

Brittle Fractures and Ductile Fractures.—Micromechanism of the Rupture of Metals. R. Calvo Rodes. (*Inst. Hierro Acero*, 1951, **4,** July–Sept., 209–219; Oct.–Dec., 304–315). [In Spanish]. The apparent differences between brittle and ductile fractures are stated. Intergranular and transcrystalline fractures and their development are considered. This development is not related to their brittle or ductile characteristics. Critical resistance to shearing and cohesion is related to the rupture of metals. Relationships between triaxiality and brittleness are studied. The theory of the 'critical kinetic energy of shear' is compared with that of 'critical shear.' The micromechanism of brittle fracture is studied and that of plastic deformation is surveyed. A general theory for the rupture of metals is proposed.—R. S.

Slip Mechanism and Workhardening of Metallic Substances. A. Kochendörfer. (*Z.V.d.I.*, 1952, **94,** Apr. 1, 267–273). Having clearly distinguished between the technological and physical approach to the plastic deformation of metal, the author presents, for the benefit of engineers, a simple survey of the physics of crystal plasticity.—J. G. W.

Notes on the Theory of the Strength of Materials. K. Matthaes. (*Z. Metallkunde*, 1952, **43,** Jan., 11–19). In most metals the ratio of the elastic shear energy to the latent heat of fusion is either close to unity or close to 2, both values agreeing with theoretical predictions. It is shown that an almost linear relation exists between the hardness and volume changes, irrespective of whether the latter are due to cold work or to alloying. The volume changes are regarded as a measure of the obstruction of slip planes by foreign atoms or by the disorder associated with cold work. The energy required to

fracture unit volume in the necked region of specimens is shown to be very little affected by heat-treatment, although the tensile strength may be greatly changed by this. From this is inferred the existence of a characteristic plastic constant, determined by the energy to cause fracture. The constancy of the specific energy to fracture is shown for an alloy steel, specimens of which were subjected to tests in the as-delivered state and after different heat-treatments. The assumption of a statistical distribution of dislocations in the slip planes of the grains, together with the assumption that the critical shear stress is determined by the density of dislocations in the slip plane leads to a straight stress/plastic-strain curve, and this was experimentally confirmed with the single crystals and polycrystalline light alloys examined, the strain being plotted on a probability scale.—P. F.

Fracturing and Fracture Dynamics. G. R. Irwin and J. A. Kies. (*Welding J.*, 1952, **31,** Feb., 95s–100s). Energy balance principles are applied to calculate the conditions which lead to rapid fracture.—U. E.

The Plastic Behaviour of Tubes under Static Internal Pressure During Disappearing Longitudinal Elongation in the Region of Finite Deformations. R. Moufang. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1942, **5,** Feb., No. 5, 65–75). In this mathematical paper formulæ are derived from which the stress/strain state of tubes of any wall strength can be calculated, when the external surface is stress-free and the inner surface subjected to a uniform hydrostatic pressure over the whole of its length. The cross-section of the tube is considered to flow plastically. The St. Venant-Mises conditions, the R. Schmidt stiffening, and the incompressibility are utilized, using stress and strain tensors. Examples of the use of the formulæ are given.—R. J. W.

Investigation of Damage to a 100-Atmospheres Pressure Vessel Made of Alloy Steel. H. Biegler. (*Technik*, 1952, **7,** Jan., 34–36). This is a case history of the intercrystalline caustic embrittlement which caused the failure of a chromium–molybdenum steel pressure vessel.—J. G. W.

Production Problems—XII; Broken Connecting Rods. (*Iron Steel*, 1952, **25,** Jan., 11, 16). This article briefly describes the metallurgical examination of two prematurely failed motor-cycle connecting rods. One rod is shown to have failed because of general weakness and low yield point, and the other from fatigue initiated by a local defect. Suggestions for avoiding repetitions of these failures are given.—G. F.

Contribution to the Study of the Tensile Strength of Plain Carbon Steels by Fluctuating Tensile Tests. H. Bühler and E. H. Schulz. (*Métaux-Corrosion-Indust*, 1952, **27,** Feb. 49–53). Systematic study has been made, using steels containing up to 1% carbon, from room temperature to 600° C., of the decohesion and tensile strength. The ratio of these two decreases almost linearly from a value of 3 for no carbon, to 1·7 for 1%. When the temperature is increased to 500° C. this ratio increases in a like manner. Variation of decohesion with temperature for different steels is similar to variation in tensile strength. Comparison of the values measured at room temperature indicates that at 500° C., as at 600° C., the reduction in tensile strength is greater than the reduction in decohesion.—B. G. B.

Dilastrain Method for Determining Endurance Limit of Materials. J. L. Rosenholtz and D. T. Smith. (*Metal Progress*, 1952, **61,** Feb., 85–88). The principle of the Dilastrain method is that the coefficient of linear thermal expansion of materials such as metals, alloys, and plastics decreases abruptly at the true endurance limit. Results are given for tests on duralumin.—J. P. S.

Torsional Fatigue Failures. J. O. Almen. (*Product Eng.*, 1951, **22,** Sept., 167–182). A number of examples of fatigue failure are given and their cause and development are described. A torsional stress diagram is developed for the analysis of surface and sub-surface stresses; this shows separately the magnitudes and distribution of biaxial tensile and compressive stress components extending from the surface to their neutral axes. Evidence is presented that the direct cause of fatigue failures from repeatedly applied torsional loads is always tensile stress; and the compressive stresses contribute only indirectly through altering the yield strength of the metal.—A. M. F.

Hardness Testing with Indenters Sensitive to Anisotropy. H. Meincke. (*Metalloberfläche*, 1951, **5,** Feb., A17–A21). The influence of various indenters in measurements of hardness anisotropy was investigated by means of measurements on single crystals and other anisotropic materials. It was found that pointed indenters as used by Knoop and Grodzinski, as well as chisel-edged indenters, were most suitable, and facilitated the derivation of tensile strength from hardness values. Microhardness readings with the Vickers pyramid give erroneous results.—P. F.

The Predetermination of the Surface Hardness of Chill-Cast Rolls from the Hardness of Small Cast Specimens and the Carbon Content. E. Diepschlag and F. H. Buch. (*Metallwirtschaft*, 1942, **21,** Dec. 25, 779–784). On the basis of simultaneous investigations of the surface hardness of chill-cast rolls and small cast specimens, a relationship between the Brinell hardness (and also the Shore hardness) and the carbon content was established. This was expressed in mathematical form, so it was possible to calculate the Brinell hardness from the Shore hardness. It was further established that the Shore hardness was influenced by the weight of the specimen. Finally, the effect of cooling velocity and roll diameter on the development of hardness was observed, and it was possible to draw graphs of the connection between roll hardness, roll diameter, and carbon content of the alloy.—R. J. W.

Comparison of the Mohs Scale with the Results of other Hardness-Testing Methods. N. Ludwig. (*Metalloberfläche*, 1951, **5,** Mar., A38–A43). The results of several hardness-testing methods are compared with the Mohs scale, on the basis of experimental results. Scratch hardness tests are unsuited for comparison; the Brinell and Rockwell scales can be compared only over the narrow range of hardness values within which these tests are applied. Both Vickers and Knoop microhardness numbers are suitable for comparison with the Mohs scale. A graph of results for these is given. A relationship given by M. M. Chruschow expresses Mohs hardness in terms of Vickers hardness by $MH = 0{\cdot}7\sqrt[3]{VH}$.

Research on Friction and Wear. F. T. Barwell. (Inst. Engineers and Shipbuilders in Scotland: *Engineering*, 1951, **172,** Nov. 23, 649–651; Nov. 30, 697–699). The author outlines steps taken in the laboratories of the Mechanical Engineering Research Organization to study the nature of wear and the manner in which it is reduced by the application of lubricants. The problems of hydrodynamic and boundary lubrication are examined in detail, and the author stresses the great advantages of the former. Descriptions are given of both experimental equipment and technique, and the results are discussed.—M. D. J. B.

Improved Machine for the Wear-Testing of Materials. Kh. N. Dement'ev. (*Zavodskaya Laboratoriya*, 1950, No. 1, 126). [In Russian]. The wear-testing machine described is a modification of the Zaitsev machine, with improved dynamometric and automatic recording mechanisms. Ferrous and non-ferrous materials can be tested for wear and friction.—S. K.

Study on Wear Phenomenon of Steel against Soil (III). T. Mitsuhashi, Y. Imai, and S. Yokoi. (*J. Mech. Lab.*, 1951, **5,** Nov. 294–298). [In Japanese]. The wear resistance of 0·1, 0·4, 0·98% C steels and that of a 0·99% C, 1·56% Cr steel against Kauto loam having a 50% moisture content was tested on a hand-drill type of wear-testing machine. The 0·98% C steel steel, quenched and tempered, had the greatest wear resistance.

Wear Tests of Carbon Steel under Low Load. K. Matsubara and T. Yoshino. (*J. Mech. Lab.*, 1951, **5,** Jan., 1–14). [In Japanese]. Wear tests on a machine of the type described by B. Kehl (*Arch. Eisenhüttenw.*, 1936, May, 563) were performed on 0·37% carbon steel, hollow cylindrical specimens at pressures ranging from 0·05 to 2·5 kg./sq. cm. and speeds from 0·4 to 3·2 m./sec. Wear in milligrammes per unit surface and distance traversed, temperature, and the coefficient of friction, were recorded for dry friction. Three types of wear are distinguished: Mechanical destruction, coherent oxidation, and quasi-oxidation. In the last case, the detritus oxidizes but not the sliding surface. Maximum wear occurred at intermediate speeds and fairly low pressure.—J. G. W.

Study for Applying Material (IX). On the Tensile Failure Mechanism of the Chain. H. Matsumoto, K. Kimura, and K. Kamada. (*J. Mech. Lab.*, 1951, **5,** Nov., 279–284). The causes of tensile failure of bicycle chains were investigated and established.—J. G. W.

The Nature of the Static and Kinetic Coefficients of Friction. E. Rabinowicz. (*J. Appl. Phys.*, 1951, **22,** Nov., 1373–1379). The variation in the value of the coefficient of friction with distance of sliding has been measured by a simple method in which a small sphere is impacted against a large block on an inclined plane. Using a load of 1 kg. and different metal

surfaces the static coefficient persists for distances of the order of 10^{-4} cm. and then gradually falls off to values corresponding to the kinetic coefficient. The action of boundary lubricants is discussed. It is shown that they can act either by diminishing the metallic interaction directly or by preventing its increase during the sliding process.—J. P. S.

The Magnetostriction and the Magnetization of Iron in a Strong Magnetic Field Taking the True Magnetization into Consideration. O. Rüdiger and H. Schlechtweg. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1942, **5,** Mar., No. 7, 87–97). The basic theory of the rotary process of magnetization and the magnetostriction of iron in high fields is considered. Earlier work by the same authors is carried a stage further by consideration of the hitherto neglected magnetoelastic energy. The corrections are small. A further increase in the magnetostriction of iron was observed at high fields. An expression for the magnetization and magnetostriction by reference to the true magnetization and the assumption of the volume dependence of magnetization is derived. The asymptotic approach to the saturation magnetostriction which exhibits a $1/H^2$ law in the usual theory, will, with reference to the volume dependence of magnetization, require a 1/H term.—R. J. W.

Non-Destructive Determining of Folds in Sheets. W. Jellinghaus and F. Stäblein. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1941, **4,** Apr.. 31–36). A fold in a steel sheet in a cross-sectional direction causes an increase in the resistance to the passage of an electric current across the sheet. A method of testing sheets containing folds is described in which both sides of the sheet are first marked out in a network of measured points. Then, by suitably arranging the two symmetrical parts of the apparatus, a current of about 10 amp. is passed through the sheets perpendicular to its plane. The resistance is determined by measuring the current and the p.d. across the sheet, using two pairs of electrodes. Several examples of the use of this method are given.—R. J. W.

The Magnetostriction of Iron in Strong Magnetic Fields. O. Rüdiger and H. Schlechtweg. (*Technische Mitteilungen Krupp Forschungsberichte*, 1941, **4,** Jan. 1–9). From thermodynamic considerations of various energies, the longitudinal effect of magnetostriction in the direction of the field is calculated as a pure rotary process. The energies considered are the external, the magnetic, the magnetoelastic, and the elastic. The equilibrium state is obtained when the sum of these energies is a minimum. An approximate law is derived relating saturation magnetostriction to the crystallographic orientations in a single crystal. Comparison with experimental results on single crystals shows that the field strengths hitherto used are too low. Expressions are then derived for the asymptobic behaviour of magnetostriction in the quasitropic polycrystalline material, which show good agreement with observed results.—R. J. W.

Permanent Magnet Steels with Preferred Magnetic Orientation. H. Krainer and F. Raidl. (*Berg- hüttenmänn. Monatsh.*, 1942, **90,** July 99–106). On the basis of theoretical considerations it is shown that considerable improvement in permanent magnet materials is possible by magnetic preferred orientation. A magnetic orientation is obtained with precipitation-hardened permanent magnet alloys with a high Curie point by heat-treating in a magnetic field. Especially suitable is an alloy with 8% Al, 14% Ni, and 24% Co, which, after heat-treating in a magnetic field, has a (B.H.) max. value of 4 to 5 × 10^6 gauss-oersteds. The composition and magnetic properties of numerous permanent-magnet alloys are tabulated.—R. J. W.

A New Magnetic Transition of Mn Ferrite. T. Okamura and J. S. Simoizaka. (*Phys. Rev.*, 1951, **83,** Aug. 1, 664–665).

The Influence of Magnetization on Ultrasonic Attenuation in a Single Crystal of Nickel or Iron–Silicon. S. Levy and R. Truell. (*Phys. Rev.*, 1951, **83,** Aug. 1, 668–669).

Magnetostriction of Various Ferrites Orientated by Heating. L. Weil. (*Compt. Rend.*, 1952, **234,** Mar. 24, 1351–1352).

Permanent Magnets. E. J. C. Patrick. (*E.S.C. News*, 1952, **5,** Spring issue, 2–6). A brief survey is given of permanent magnet materials, and their applications in industry are briefly reviewed.—J. P. S.

Magnets. M. Allec. (*Mét. Constr. Mécan.*, 1951, **83,** Nov., 881–887). The author discusses the development and application of anisotropic and isotropic magnets. Their properties are reviewed.—R. S.

Magnetic Properties of Amalgams of Ferrous Metals. F. Pawlek. (*Z. Metallkunde*, 1950, **42,** Dec., 451–453). Electrolytically deposited iron and cobalt do not form amalgams with mercury cathodes but suspensions of fine particles, which, in the form of a pyrophoric powder obtained by removal of the mercury by vacuum distillation, exhibit permanent magnetism. Measured intensities are below those given by Weil, probably owing to the conditions under which the powders were made.—P. F.

The Cause of Change in Magnetic Saturation of Iron–Nickel–Aluminium High-Coercivity Alloys During Annealing. O. S. Ivanov and Yu. M. Kazimirov. (*Doklady Akademii Nauk S.S.S.R.*, 1951, **81,** 1, 35–38). [In Russian]. From experimental evidence it is suggested that during annealing the transformation of iron into the paramagnetic phase β_2 lowers the magnetic saturation of the above alloys.—V. G.

The Influence of Composition on the High Coercive State of Iron–Nickel–Aluminium Alloys. O. S. Ivanov, Yu. M. Kazimirov, and O. A. Novikova. (*Doklady Akademii Nauk S.S.S.R.*, 1951, **81,** 2, 231–234). [In Russian]. The influence of composition and heat-treatment on the coercive force and magnetic saturation of iron–nickel–aluminium alloys was investigated.—V. G.

The Magnetization Process in Ferrites. J. J. Went and H. P. J. Wijn. (*Physical Rev.*, 1951, **82,** Apr. 15, 269–270). The authors describe measurements of permeability of ferrite as a function of field strength and frequency of reversal of the field. They conclude that two separate magnetization processes are involved in magnetizing high-permeability ferrites: first, a pure rotation of electron spins, which is independent of field strength; and secondly, irreversible displacements of the ferrite Bloch wall.—E. T. L.

A Two-Fluxmeter Method of Measuring Ferromagnetic Hysteresis Loss. H. Aspden. (*J. Sci. Instruments*, 1952, **29,** Jan., 5–7). A method of recording the ferromagnetic hysteresis loss is described using two fluxmeters, the second to integrate successive electrical discharges, which are proportional in magnitude to the magnetizing field. It is shown that the time for measurements can be reduced to a small fraction of that normally taken by the reversals or step-by-step methods, without loss of accuracy.—H. D. W.

On the Dynamic Characteristics of the Magnetostriction Alloy 'Alfer.' H. Masumoto and G. Ôtomo. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1950, **2,** June, 413–419). [In English]. The dynamic characteristics of the Fe–Al magnetostriction alloys ranging from 6·36 to 14·38% Al have been measured by the bridge method in the fields of 5, 10, 15, and 20 oersteds. The magnetostrictive activity and sound velocity in the field of 10 oersteds are at a maximum and minimum respectively between 12·2 and 13·4% Al, whereas max. static magnetostriction occurs in the range 11·5–13·2% Al. The magnetostrictive activities of these alloys are considerably increased by small additions of nickel.—J. G. W.

On the Ferromagnetic Resonance Absorption in Magnetite Single Crystals at 9400 MC and 4560 MC. T. Hirone, H. Watanabe, J. Mizuno, and N. Tsuya. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1950, **2,** Oct., 774–779). [In English].

On the Change of Reversible Susceptibility of Ferromagnetic Substances Due to Tension. T. Katayama and N. Kunitomi. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1950, **2,** Feb., 22–28). [In English]. Theoretical calculations of the reversible susceptibility as a function of magnetization under various applied tensions were based on Kersten and Döring's internal stress theory of ferromagnetic substances. There is qualitative agreement with experimental data.—J. G. W.

On the Magnetostriction of Iron–Aluminium Alloys and a New Alloy 'Alfer.' K. Honda, H. Masumoto, Y. Shirakawa, and T. Kobayashi. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1949, **1,** Dec., 341–347). [In English]. From measurements of magnetostriction and intensity of magnetization at room temperature, and in fields of less than 1200 oersteds, results for iron obtained by others were confirmed. From the study of 17 Fe–Al alloys, containing up to 16·56% Al, increasing the aluminium content causes the positive maximum value of magnetostriction to increase, and reduces its negative value. The latter disappears in alloys containing more than 5·90% Al, the maximum disappears in alloys with more than 8·80% Al; this also depends on the field strength. In a field of 1100 oersteds the intensity of magnetization decreases with increasing aluminium. The 13·14% Al alloy has a magnetostriction of 40 × 10^{-6} in a field of 1200 oersteds and is suitable as a supersonic oscillator; the name 'Alfer' is given to it by the authors.—J. G. W.

An Improved Type of Thickness Tester. K. Kamiyoshi. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1949, **1**, Oct. 335–339). [In English]. Stevenson's method of thickness measurement by magnetization has been modified, and a comparator instrument based on this is described.—J. G. W.

On the Internal Stress and the Internal Friction of Metals. II—The Change of the Internal Friction of Ni_3Fe During the Formation of Superlatice. H. Sato. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1949, **1**, Oct., 207–211). [In English]. Measurements showed that during the initial stage of superlattice formation, internal friction decreases more quickly than the square of the initial permeability, which corresponds to the associated magnetic changes.—J. G. W.

A Magnetic Sorting Bridge. (*Wire Ind.*, 1951, **18**, Dec., 1066–1067). This is a simple description of the operating principle and the uses of the magnetic sorting bridge as developed by the G.E.C. in co-operation with the Aero Engine Division of the Ford Motor Co. Particular reference is made to the testing of aero-engine valve springs.—J. G. W.

Magnetic Properties of Rhombic Ferric Oxide ($Fe_2O_3\alpha$). R. Chevallier. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 172–188). [In French]. The magnetic properties of ferric oxide consist of a fundamental paramagnetism varying with temperature, and a ferromagnetic component which disappears at the second-order transition point, 675° C. In intense fields the magnetization is reversible and the superposition additive, but in fields of several thousand gauss, there is a substantial irreversible component. Single crystals of α-Fe_2O_3 are rhombic and paramagnetic along the main axis, but isotropic and ferromagnetic at right-angles to it. The properties of a uniform grain-size powder of the oxide depend on the grain size, with the ferromagnetic component decreasing as the grain size decreases. The author points out the possibility of impurities (*e.g.*, oxygen) causing the ferromagnetism.—E. T. L.

Magnetic Properties of Ferrites. J. L. Snoek. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 228–238). [In French]. The crystal magnetic energy of Fe_3O_4 is equal to 10^5 ergs./c.c., which is so large that it prevents the initial permeability being great. This is related to the author's measurements of permeability. He then considers a model explaining the properties of magnetite. Above 120° K., electrons of the bivalent iron present are thought to become mobile. Gamma-Fe_2O_3 forms a solid solution with Fe_3O_4, but this is unstable because of the existence of vacant sites in the Fe_2O_3. $LiFe_5O_4$ is stable because the number of ions is just sufficient. The author explains the absence of ferromagnetism in $ZnFe_2O_4$ and $CaFe_2O_4$, and the enhanced ferromagnetism of $NiFe_2O_4$ and $MnFe_2O_4$. All ferrites except Fe_3O_4 have negative magnetostriction, so that adding this to another ferrite gives a substance of zero magnetostriction.

Paramagnetism of the Ferrites of Iron, Cobalt, and Nickel. M. Fallot and P. Maroni. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 256–257). [In French].

The Effect of Thermal Expansion on the Value of the Curie Coefficent for Ferrites. L. Néel. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 258–259). [In French].

The Electrical Resistance of Some Ferromagnetic Metals Under the Influence of a Magnetic Field at Low Temperatures. C. J. Gorter. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 279–280). [In French]. With ferromagnetic alloys the field's orientation with respect to the direction of an electrical current through them alters the resistance considerably, at the temperature of liquid hydrogen. With pure metals, however, this orientation effect remains slight.—E. T. L.

The Gyromagnetic Magneto-Mechanical Properties of Some Ferromagnetic Materials of the Iron Group. A. J. P. Meyer. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 303–304). [In French].—E. T. L.

Influence of Order on Magnetic Properties. R. Smoluchowski. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 389–398). [In English]. A new theory of magnetic saturation in binary alloys, based on a consideration of the concentration variations of the electrons in equivalent groups of atoms is presented. In the case of a body-centred-cubic lattice, these groups include first and second neighbours, and the theory is in accord with experimental data for Fe–Co. For face-centred-cubic structures such as Fe–Ni, the group consists of only first neighbours. The theory allows a calculation of the effect of order on magnetic properties, including the Curie temperature, magnetic anisotropy, permeability, and the coercive force. Finally the author discusses the effect of the magnetic properties on the phenomena due to order.

Experiments on a Specimen with Large Domains. K. H. Stewart. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 325–331). [In English]. A single crystal of ferrosilicon was made so as to form large magnetic domains. Its hysteresis cycle mainly consisted of only one Barkhausen step ; that was studied in detail and discussed in terms of the motion of the domain walls.—E. T. L.

Atomic Moments and the Curie Points for Iso-Electronic Alloys of the Iron Group with Face-Centred-Cubic Structure. P. Taglang. (Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble : *J. Phys. Radium*, 1951, **12**, Mar., 414–417). [In French]. The author shows a linear relationship between Curie point and atomic moment for various alloys having the same electronic rank. A considerable extrapolation of the results defines the moment for the Curie temperature of absolute zero. This extrapolated moment is the ferromagnetic moment, and is linearly related to the electronic rank.—E. T. L.

Some Aspects of the Propagation of Ultrasonic Waves. A. Bouvier. (*Ingénieurs et Techniciens*, 1952, Feb., 37–39). Methods of producing ultrasonic waves, and the experimental determination of absorption coefficients are given.

Physico-Metallurgical Considerations in Ultrasonic Testing. H. J. Seemann. (*Metall*, 1951, **5**, Dec., 531–537 ; *Métaux-Corrosion-Indust.*, 1952, **27**, Jan., 14–23). The author compares the wavelengths of realizable elastic vibrations with the dimensions of typical structural constituents and discusses the problem of absorption and scatter of elastic waves in solids, by reference to experimental knowledge. He concludes that the influence of structure on the spread of ultrasonic waves is unmistakable and probably accounts for the anomalies encountered in the listing of steel specimens, as reported by Bastien and co-workers. He recommends further study of the absorption of elastic waves in solids.—J. G. W.

The Belgian Method for the Ultrasonic Testing of Materials. G. A. Homes, Y. Ots, and E. Symon. (*Métaux-Corrosion-Indust.*, 1952, **27**, Jan., 24–33). The difficulties in obtaining a satisfactory contact on the material to be tested are discussed and practical solutions to the problem are described. Methods of testing pipes, castings, and plates are illustrated. A description is given of the ultrasonic testing of the components of a cyclotron, the yokes of which weigh 25 tons each.

Testing of Railroad Rails by the Ultrasonic Resonance Method. P. K. Bloch. (*Non-Destructive Test.*, 1951–52, **10**, Winter, 16–18). The method has been developed to examine rail ends in the vicinity of fishplate bolt holes ; it employs a thickness gauge. The ultrasonic waves cause audible signals in the operator's headphones, the frequency of which indicates various types of flaw.—P. M. C.

Railroad Maintenance Inspection. A. S. Pedrick. (*Non-Destructive Test.*, 1951, **10**, Autumn, 38–43). The author describes the types of equipment used to detect internal and surface flaws by the Southern Pacific Railroad Co. The ultrasonic reflectoscope, gamma-ray radiography, magnetic particle, and fluorescent penetrant crack detection methods are dealt with.—P. M. C.

The Detection of Internal Defects with the Aid of Ultrasonic Images. R. Pohlman. (*Métaux-Corrosion-Indust.*, 1951, **26**, Oct., 410–414). A new method is described whereby a visual image of structural defects is obtained. The principle is as follows : the metal, in sheet form, is immersed in a tank of water and a source of ultrasonic vibration placed close behind it. The ultrasonic waves are focused by a mirror through the metal on to a simple lens, also immersed in the water tank about 6 ft. 6 in away. The beam is focused by this lens to give an image of the specimen on a thin hollow cell containing a suspension of aluminium powder. Under ultrasonic excitation, the aluminium particles orientate themselves with respect to the side of the cell and, if illuminated optically, an 'image' of the irradiated specimen can be obtained and any internal defects can be observed.—B. G. B.

A New Apparatus for Ultrasonic Testing and Its Practical Application. J. Krautkrämer and H. Kraut-Krämer. (*Métaux-Corrosion-Indust.*, 1952, **27,** Feb., 89–94). A method based on reflection of ultrasonic waves from internal defects is described. The reflected wave produces a trace on a cathode-ray tube, which is then recorded photographically. The method can be used on steel specimens up to 500 cm. thick. Photographs are reproduced showing how flaws can be detected by this means.—B. G. B.

Ultrasonic Testing of Rail Vehicle Axles. E. Martin. (*Stahl u. Eisen*, 1952, **72,** Feb. 14, 176–185). Tests have shown that fissures in that part of an axle lying in the wheel hub, and not previously detectable, can be found with certainty by ultrasonic methods. The depth of vertical fissures and the area of fatigue cracks can be estimated with sufficient accuracy. The use of oblique radiation to detect both external and internal fissures is described. [A translation is in course of preparation].—J. P.

Non-Destructive Testing As Applied To Tank Parts Inspection. J. K. McDowell. (*Non-Destructive Test*, 1951–52, **10,** Winter, 14, 15). This is a very brief review of the standard methods of testing used to examine various engine parts of American tanks.—P. M. C.

Magnetic Particle Inspection. C. M. Geist. (*Non-Destructive Test.*, 1951–52, **10,** Winter, 27, 28). The author lists the many aircraft parts which are subjected to magnetic inspection at the Lockheed Aircraft Corp., California. Typical flaws in some of these are described.—P. M. C.

Magnetic Particle Inspection of Jet Engine Parts. A. Robinson. (*Non-Destructive Test.*, 1951–52, **10,** Winter, 19–23). The author discusses general principles and practices employed at the Thomson Laboratory of the General Electric Co., Massachusetts.—P. M. C.

Magnetic and Electric Methods for the Non-Destructive Inspection of Metal Parts. W. Jellinghaus. (*Métaux-Corrosion-Indust.*, 1952, **27,** Jan., 34–43). Methods of measuring magnetic permeability are described. The application of this principle to the inspection of rods and tubes by a differential process of comparison with a standard is shown. A method for use with stainless steels (if purely austenitic) involving the measurement of the inductive resistance is described. Magnetic methods for determining the depth of cementation, and detecting cracks are also dealt with. A method in which eddy currents are measured is said to be particularly suitable for detecting errors in thermal treatment.—B. G. B.

Experiences in Non-Destructive Testing. K. Matthaes. (*Metall*, 1951, **5,** Dec., 544–546). This is a review of the non-destructive testing carried out at the works of Ernst Heinkel A.G., showing its advantages compared with conventional mechanical and chemical tests.—J. G. W.

Testing by Non-Destructive Methods. R. Hammond. (*Overseas Eng.*, 1952, **25,** Mar., 274–276; Apr., 322–324). Recently developed practices, including spectrum analysis, ultrasonic flaw detection, brittle lacquer coatings, and electric resistance strain gauges, are reviewed. Details are given of the use of the last to measure stresses in aircraft propellers and gas-turbine blades. The use of mobile industrial X-ray equipment for examining welds in shipyards and of the smaller and more convenient gamma-ray sources is described.

Rational Method for the Surface-Quality Control of Valve Springs. V. B. Raitses. (*Zavodskaya Laboratoriya*, 1950, No. 1, 123–124). [In Russian]. The disadvantages of the magnetic-powder method of testing valve springs for fine cracks or other surface defects, when the magnetization is carried out in batches between common contact discs, are outlined. An improved procedure is described, in which a separate circuit is used for magnetizing each spring. The improvement in the visibility of defects by the previous electrolytic deposition of 7–10 μ of zinc followed by heating to 160–180° C. is illustrated.—S. K.

Theoretical and Practical Sensitivity Limits in Fluoroscopy. D. T. O'Connor and D. Polansky. (*Non-Destructive Test.*, 1951, **10,** Autumn, 10–21). Expressions are developed which describe the sensitivity or quality of fluoroscopic images in terms of measureable characteristics of X-ray tubes and fluoroscopic screens. Experimental data are presented in support of the expressions. The requirements imposed by adequate fluoroscopic viewing are used to specify the design features of a proposed fluoroscopic X-ray tube. (49 references).—P. M. C.

Fluorescent Penetrant Inspection of Jet Propulsion Engine Components Parts. W. B. Buckman. (*Non-Destructive Test.*, 1951–52, **10,** Winter, 11–13). This method, which is used to detect surface flaws in non-magnetic materials, makes use of the fluorescence exhibited by certain chemical compounds when examined by 'black' light. Such compounds can be introduced into surface flaws.—P. M. C.

Simple Method of Determining Depth and Location of Defects by Fluoroscopy and Radiography. Sh. S. Manevich and B. V. Borshchev. (*Zavodskaya Laboratoriya*, 1948, **14,** 2, 202–203). A simple method of determining the depth of defects in castings is described.—V. G.

The Most Recent Development in the Non-Destructive Testing of Materials and Tools. R. Berthold. (*Berg- hüttenmänn. Monatsh.*, 1941, **89,** Jan., 1–3). With the recently developed counting tube and ancillary apparatus, rapid measurements of weak intensities from a source of X-rays or γ-rays is possible. This technique can be used for thickness measurements, investigating pores and shrinkage cavities in cast metals, and testing the safety of X-ray installations. Non-destructive testing by magnetic induction is discussed and the automatic recording of tests on wire is described as an example. Finally, the technique of micro-radiography is described in which the metallographic structure is demonstrated by passing X-rays through a segregated specimen, which absorbs the X-rays differentially.—R. J. W.

The Applications of X-Rays in Foundry Practice. Z. Debinska. (*Przeglad Odlewnictwa*, 1952, **2,** Mar., 87–100). [In Polish]. Methods using X-rays and γ-rays in foundry practice are described.—V. G.

Method of Sorting Steels Based on Sign of Thermoelectric Effect. S. V. Skorikov, A. I. Askenazi, and M. V. Dekhtyar. (*Zavodskaya Laboratoriya*, 1945, **11,** 1, 95–98). A method and apparatus for rapid identification and separation of Cromansil steel from other carbon and alloy steels based on the sign of thermoelectric force are described.—V. G.

Measurements on Thin Iron Films. A. van Itterbeek, L. De Greve, and F. Heremans. (*Appl. Sci. Res.*, 1952, **2,** Section B, 320–324). Curves are established for the specific resistance as a function of thickness for iron films obtained by spattering or condensation in a vacuum respectively. The curves obtained with these two techniques are completely different. Electron microscope and electron diffraction pictures of the films are given.—J. P. S.

The Problem of the Limit to Which Hot Steels Can Be Stressed. C. A. Duckwitz. (*Berg- hüttennmänn. Monatsh.*, 1942, **90,** Aug., 111–119). The fatigue limit has proved to be of use in calculations for boiler installations operating at up to 500° C. Efforts should be made to obtain data valid at 800° C., as, until this is done, safety factors higher than necessary must be utilized. It is shown that a slightly hardened Mn–Si steel can be used instead of the molybdenum steels having tensile strength ranges of 38–48 and 45–55 kg./sq. mm. These Mn–Si steels have a greater creep strength up to 450° C. than the molybdenum steels, but at 500° C. they exhibit a steep fall in creep strength. A molybdenum-free Cr–V steel has been developed to replace Cr–Mo steel for use at above 500° C., and shows considerable promise.

A General Basis for the Production and Development of Heat-Resisting Heat-Treated Steels. H. Scholz and W. Holtmann. (*Mitteilungen der Kohle- und Eisenforschung*, 1941, **3,** Feb., 1, 47–58). From a consideration of the γ-region of binary alloys of iron and of ternary alloy systems, the authors derive a rule by which a certain carbon content gives a highest value for the upper transformation temperature in heat-resisting steels. The fatigue strengths of such steels are plotted against the percentages of the constituent elements in a variety of ways. By their arguments, the authors claim that the uneconomic overalloying of steels can be avoided and that, within specified limits, alloying elements can be exchanged for others without reducing the strength properties of the steels. Simultaneous observation of the fine structure enables the correct heat-treatment to be found.—R. J. W.

Considerations on Creep. A. Fotiadi. (*Métaux-Corrosion-Indust.*, 1952, **27,** 69–74). Knowledge of the mechanical properties of alloys at high temperatures is primarily based on their behaviour in static creep tests. The author considers that since machine parts are often subjected to rapid or continuous variations in vibration, deforming forces, and heat, the results of these changes on the metal structure should be taken into account. The safe use of alloys in machines is said to depend more on the ability to resist these sudden fluctuations than on normal changes.—B. G. B.

Rheological Considerations on the Creep of Steel. H. Umstätter. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 119–126). The applicability of rheological considerations to the mechanical behaviour of material is discussed, and it is shown that viscosity and relaxation time are better criteria than the usual concepts such as elastic moduli used in physical testing. The connection between the values used in rheology is given by Maxwell's general law of matter, $G\theta = \eta$, where G is the transverse modulus of elasticity, θ is the relaxation time, and η is the viscosity. From the general law, a mathematical relationship is derived between stress, deformation, and time, which can be illustrated as a family of creep curves on a three-dimensional diagram. The creep curve valid for certain experimental conditions can be extrapolated to long periods only if the constants in the mathematical relationship are known with accuracy for the material under consideration. An experimental apparatus is described for determining these constants for steel. The steel, as a wire, is stretched inside a thermostatted steel cylinder and vibrated at its characteristic frequency. This frequency is compared with that of a standard tuning fork, the two frequencies being applied to the plates of a cathode-ray oscilloscope. When the frequencies are equal, the resulting Lissajou figure is stationary, but as relaxation sets in, the figure begins to rotate. From the angular velocity of rotation it is possible to calculate the change in frequency and thus the relaxation. It is pointed out that rheological considerations of creep apply to cases where the changes occur only through a flow process and not when they are caused by diffusion or recrystallization.—J. P.

Factors Influencing the Creep Resistance of Wrought Carbon Steels. C. H. M. Jenkins and H. J. Tapsell. (*J. Iron Steel Inst.*, 1952, **171**, Aug., 359–371). [This issue].

Heat-Resisting Materials—Some Factors in the Creep Resistance of Heat-Resisting Austenitic Alloys. X. Waché. (*Métaux-Corrosion-Indust.*, 1952, **27**, Feb. 56–68). The microstructure of austenites is an essential factor in their resistance to creep and depends on all their previous thermal and mechanical history. A precipitated phase in a finely divided form is more advantageous than a coalesced phase. Study of carburized austenites is relatively simple and the results obtained have led to a better knowledge of the laws governing precipitation. These results have been successfully applied to austenitic alloys and have enabled a reduction in the amount of rare alloying elements to be made, owing to a clearer understanding of the process.—B. G. B.

The Modern High Quality Steels. F. Rapatz. (*Berg-hüttenmänn. Monatsh.*, 1940, **88**, Sept., 109–115). The production of the various alloying elements in Germany, U.S.A., Russia, Great Britain, and the British Empire are first given and compared. Necessary economies in the use of alloying elements, including cobalt, vanadium, molybdenum, and tungsten, which were not available to Germany led to the development of new high-speed steels. The high-temperature strength and fatigue limits of chromium–nickel and chromium–manganese steels are compared at temperatures up to 900° C.; similar graphs are given for various tungsten steels. The production of ferromanganese from iron ore containing manganese, and that of vanadium from vanadium-bearing iron ore are given as examples of the ingenious ways the Germans overcame their difficulties.—R. J. W.

Structural Carbon Steels with an Addition of Boron. (*Avtomobilnaya Promyshlennost*, 1946, No. 7–8, 18–19). An investigation of the mechanical properties of boron-treated structural steels, containing 0·2 and 0·4% of carbon is described.

Rôle Played by Boron in the Fibrous Fracture of Heat-Treatable Steel. S. I. Sakhin, N. N. Rodionov, N. G. Vergazov, and A. D. Gurasov. (*Stal*, 1946, **6**, 11–12, 666–672). An investigation of the influence of boron on: (1) The austenite transformation during quenching; (2) the susceptibility of boron-treated steel to temper brittleness; and (3) the development of heat-treatable constructional steels is reported.

English Use Boron in Normalized and Drawn Heavy Sections. W. E. Bardgett. (*Iron Age*, 1952, **169**, Jan. 10, 81–84). In studies made at the United Steel Companies, boron has been added to low-carbon low-alloy steels to obtain high ultimate tensile stress and yield-stress values in the as-rolled or normalized condition. Tests have been carried out on the effect of boron in the presence of molybdenum. With 0·15% of molybdenum in a 0·14% C steel the effect was negligible, but at 0·44% molybdenum the ultimate tensile strength was increased 48% and the yield stress more than doubled.

The Effect of Vanadium, Molybdenum, Silicon, and Carbon on the Strength Properties, especially the Fatigue Strength of Heat-Treated Steels. W. Holtmann. (*Mitteilungen der Kohle- und Eisenforschung*, 1941, **3**, Feb., No. 7, 1–46). A systematic examination of the changes in fatigue strength of heat-treated alloy steels (C 0·02–0·5%, V 0·2–5·5% or Mo) was carried out. The effect of carbon and silicon on molybdenum–vanadium steels was also examined. Increasing the alloy content to the limit of the γ-region increased the fatigue strength to a maximum. It is shown how carbon improves the fatigue strength, and, lowering the critical cooling rate, suppresses the formation of ferrite, by widening the γ-loop. The tensile strength and ultimate strength at different temperatures are affected in a manner similar to the fatigue strength. In molybdenum–vanadium steels, molybdenum, vanadium, and carbon affect the texture in a manner similar to the simple alloy steels.—R. J. W.

The Effect of Alloy Elements on the Heat-Treatment of Grey Cast Iron. M. M. Hallett. (*Alloy Metals Review*, 1952, **8**, Mar., 2–8). The effects of alloying elements on the response to heat-treatment of grey cast iron is studied. Nickel decreases the stability of iron carbide, retards the breakdown of pearlite to form ferrite and graphite, and promotes deep hardening on oil-quenching. Chromium increases the stability of iron carbide, assists the prevention of breakdown of pearlite, and probably promotes hardenability when it is present in solid solution in the iron. Molybdenum increases strength in the as-cast condition and retards both the breakdown of pearlite and ferrite and the transformation of austenite to pearlite. Irons with an addition of both nickel chromium and molybdenum harden effectively in heavy sections.—J. P. S.

Heat Treated Hollow Drill Steel. W. Stich and W. Blüthgen. (*Berg- hüttenmänn. Monatsh.*, 1943, **91**, Jan., 1–3). The texture and fractures of tempered and primarily heat-treated hollow drill steel are compared. The method of Vereinigte Oberschlesische Hüttenwerke in which hollow drill steel was hardened immediately from the roll heat was compared, from a metallurgical and technical viewpoint, with the usual tempered steels of similar composition. In practice, this treatment yielded an improvement in the cutting properties of about 80%. The resistance of shafts for rock borers, made from such primary heat-treated hollow drill steel, to impact and fatigue fracture is similarly considerably larger.—R. J. W.

The Mechanical Properties of Large Forgings and Influencing Them by Segregation and Forging. W. Coupette. (*Mitteilungen der Kohle- und Eisenforschung*, 1940, **2**, Dec., 6, 189–237). The mechanical properties of large forgings and the effect of segregations and of forging on them were investigated first with a carbon steel (C 0·4%, Mn 0·9%) and then with a high alloy Cr–Ni–Mo–V steel. The investigations were carried out in such a way that the effect of the initial structure, the segregations and the forging were first separated from each other. The effect of a soaking anneal was not considered. The notched bar impact strength is decreased only a little by segregations, whilst the yield point is not affected. The unfavourable effect of segregations is not diminished by heavy forging. Careful attention must be paid to the heavily segregated areas.—R. J. W.

The Conditions of Stress and the Life of Wire Ropes. R. Posselt. (*Berg- hüttenmänn. Monatsh.*, 1942, **90**, Oct., 151–158). The stress conditions and life of hoisting cables in connection with the cable strengthening and the residual elongation in works is described. Idealized cases are considered from first principles, then the effect of use on the residual change in length of six Koepe-Rund cables from a pit hauling plant is shown diagramatically.—R. J. W.

Steel Wire Ropes: Some Factors Influencing Their Life. A. E. Williams. (*Iron Coal Trades Rev.*, 1952, **164**, Jan. 25, 187–191). The author briefly discusses the production of steel wire ropes and the materials used in their manufacture. Some of the factors affecting their life, including bending stresses, corrosion, and fatigue, and matters relevant to their proper maintenance, are also considered.—G. F.

The Effect of Quenching from the Heat of Rolling on the Properties of a Chromium Manganese Steel Alloyed with Vanadium. A. Legat and E. Plöckinger. (*Berg- hüttenmänn. Monatsh.*, 1942, **90**, Aug., 119–126). With a Cr–Mn–V steel, the effect of various modes of tempering on the mechanical values was investigated. Quenching in oil was carried out (*a*) immediately from the heat of rolling (or forging), (*b*) from

40° C. above the Ac_3 point, and (*c*) from 140° C. above the Ac_3 point. It is shown that the strength and stretching limit values were considerably increased after quenching immediately from the heat of rolling.—R. J. W.

New Economy Case-Hardening Steels: En 351–En 355 and En 361–En 363 (B.S. 970). (*Iron Steel*, 1952, **25,** Jan., 8). This article summarizes the compositions, properties, and outstanding features of the new 'emergency' steels En 351, En 355, and En 361–En 363 (B.S. 970), developed to replace the 2–5% Ni case-hardening steels En 33–En 39 and En 325.

Conventional Designation of Alloys. C. Chaussin. (*Mét. Constr. Méc.*, 1952, **84,** Feb., 89–91). The letters and numbers used in the French steel standards are explained with examples.

Steels for Surface Hardening. H. Bühler. (*Métaux-Corrosion-Indust.*, 1952, **27,** Feb., 54–55). A list of American and French steels suitable for surface hardening is given in two tables of analyses.—B. G. B.

Comparative Table of Stainless Steel Specifications. (*Acciaio Inossid.*, 1951, **18,** Nov.–Dec., 16–17). [In Italian]. A table is given comparing the principal characteristics of Italian 'Avesta' stainless steels with those of the Swedish, American, French, German, and British equivalents. The Avesta electrodes recommended for use in welding these steels are listed.

Rust-Resisting Steels—Heat-Resisting Steels. (Published by Soc. d'Electro-Chimie, d'Electro Métallurgie et des Aciéries Electrique d'Ugine, 1951). This book of 188 pages gives comprehensive information on the products of the Ugine Company. Corrosion in the hot and cold states and the resistance of steels to water, steam, acids, and alkalis are discussed. The second half of the book deals with the properties and applications of the martensitic and ferritic steels with the initial code letters PM, FI, S, R, and F; the austenitic steels of the NS series; and 'Inoxargent' a special stainless steel (C 0·07, Cr 13, Ni 13%) intended for artistic work by the silversmith.—R. A. R.

Improvements in Quality of Deep Drawing Sheet Steel. T. F. Olt and R. S. Burns. (*Metal Progress*, 1952, **61,** Feb., 51–56). Advancements in the rate of production and quality of deep-drawing steel sheets during the last 25 years are outlined, and the greater uniformity in the properties of aluminium-killed steel as compared with rimming steel is commented on.—R. A. R.

Mechanical Properties of Flame-Hardened Caterpillar Track Pins. A. W. Grönegress. (*Z.V.d.I.*, 1952, **94,** Mar. 11, 231–233). This is an account of tests in which hardness, bending resistance, impact strength and fatigue limit of flame-hardened caterpillar track pins were investigated.—J. G. W.

Investigation of the Bursting Strength of Safety Discs. A. Biegler. (*Technik*, 1952, **7,** Feb., 74–76). The author does not recommend the use of notched discs of ductile metals, but thinks it advantageous to use discs of brittle cast iron. J. G. W.

Properties of Modified Cast Iron. J. Piszak. (*Przeglad Odlewnictwa*, 1952, **2,** Mar., 79–87). [In Polish]. A definition for modified cast iron is proposed. The influence of the structure of this iron on its mechanical and technological properties is outlined, and the results of the investigation of the mechanical and casting properties are tabulated.—V. G.

A Study of Some Properties of Spheroidal Graphite Cast Iron. M. Ballay, R. Chavy, and J. Grilliat. (*Fonderie*, 1951, Aug.–Sept., 2589–2604; Oct., 2636–2652). The manufacture and properties of nine casts of spheroidal-graphite cast irons are discussed. They were specially made because, although there is a mass of documentation on these irons, the French metallurgist generally finds that the data quoted are not based on the type of test specimens with which he is familiar.—R. S.

Application of Iron Castings in the Metallurgical and Engineering Industries. Improvement of Products by the Use of Special Ferrous Alloys. (*Mét. Constr. Méc.*, 1951, **83,** Dec., 977). The limitations of grey cast irons, especially as regards resistance to mechanical stresses, high temperature, and corrosion are indicated.—R. S.

The Chemical-Physical Laboratory of Krupp-Grusonwerk. O. Keune. (*Technische Mitteilungen Krupp, Technische Berichte*, 1941, **9,** May, No. 3, 49–63). An historical description of the growth of the chemical-physical laboratories is followed by a description of the wide scope of work undertaken at these well-equipped laboratories. Routine X-ray inspection of welded and cast structures, the use of a wide variety of mechanical testing machines, and the usual chemical methods are described.—R. J. W.

METALLOGRAPHY

The Reflected-Light Phase-Contrast Microscope and Its Use in Metallography. F. Gabler and R. Mitsche. (*Arch. Eisenhüttenwesen*, 1952, **23,** Mar.–Apr., 145–150). The theories of the transmitted and reflected light phase-contrast microscopes are presented and the possible applications of the latter in metallography are discussed. A modern reflected-light phase-contrast equipment, which requires no special objective and in which the change from phase contrast to clear field illumination is possible by moving the phase plate, is briefly described. Differences in height of 10–50 Å. on a specimen give clearly visible differences in intensity when observed under conditions of phase contrast. The principal uses of the phase-contrast microscope in metallography concern the rendering visible of the relief in microsections, the observation of phase contrast in etched sections, and, if necessary, the use of phase change on reflection. Illustrations are presented, showing the structure of ledeburitic tool steel, pearlitic cast iron, heat-treatable steel, bronze, and copper–oxygen and aluminium–silicon alloys.—J. P.

How to Obtain Good Micrographs at High Magnification—Some Optical Aspects. S. Modin and L.-E. Eriksson. (*Jernkontorets Ann.*, 1952, **136,** Jan., 1–8). [In Swedish]. Using a Reichert microscope MeF equipped with an arc lamp and specimens of a eutectoid carbon steel, investigations were made on the effects of different objectives, filters, and immersion oils on the quality of the micrographs obtained. A 2-mm. apochromat objective gave good pictures with either a yellow, green, or blue filter. The other objectives gave good results only with the yellow or green filter. Focusing was easiest with a yellow filter when the image on the ground glass was illuminated through it. There was scarcely any difference in the resolution obtained with the different objectives having the same numerical aperture. Of four immersion oils, a pure cedar oil and Aris immersion oil No. 1515 gave the best results.—R. A. R.

A High Resolution Surface-Profile Microscope. S. Tolansky. (*Nature*, 1952, **169,** Mar. 15, 445–446). A development of the Schmaltz light slit microscope is described. The slit is replaced by a coarse graticule of parallel dark lines giving reversed illumination and a multiple profile picture. The resolution will permit precision measurements of hardness indentation depths.—A. G.

Electrolytic Polishing of Microscope Specimens. J. W. Holleman and W. A. Schultze. (*Metalen*, 1951, **6,** Aug. 31, 306–311). [In Dutch]. After reviewing current theories of electrolytic polishing, the anodic polishing of micro-specimens is discussed.—R. S.

Metallographic Detection of Temper Brittleness in Heat-Treating Steels. H. Klemm. (*Stahl u. Eisen*, 1951, **71,** Nov. 8, 1264–1265). The possibility of using alkaline potassium permanganate solution as an etchant for detecting temper brittleness in steel is examined. After etching for 1 min. at 70° C. in a solution of cold-saturated potassium permanganate plus 10% potassium hydroxide, very faint fine dark dots could be detected. When viewed in incident light and dark field illumination the pattern was much more distinct. This solution could be used to separate tough specimens from temper-embrittled ones. Micrographs show some of the results obtained.—R. A. R.

The Problem of Determining the Grain Size of Steels with Special Reference to Pearlitic Carbon Steels. A. Legat and K. Schlacher. (*Berg- hüttenmänn. Monatsh.*, 1942, **90,** June, 71–78). From the determination of the so-called 'inherent' grain size in case-hardened steels (McQuaid and Ehn), proposed methods were investigated with regard to their applicability for pearlitic steels. Furthermore, the customary methods for grain-size determination in pearlitic steels were compared practically, and then critically considered. A combined oxidation etching procedure, followed by viewing in polarized light, was found to be most satisfactory for the workable grain size in pearlitic steels.—R. J. W.

A New Primary Etching Medium for High Alloy Austenitic Steels. E. Plöckinger and A. Legat. (*Berg- hüttenmänn. Monatsh.*, 1939, **87,** Nov., 202–203). The use of a newly developed primary etching medium to replace *aqua regia* is described. It consists of 1 g. picric acid dissolved into a saturated solution with 96% alcohol and the total volume doubled with concentrated HCl (1·19). Photographs are given as examples of the use of this etch on castings of high-alloy austenitic steels.—R. J. W.

Etching Processes. (*PERA Bulletin*, 1952, **5,** Mar., 95–97). A solution for etching stainless steel contains 20 g. of ferric chloride and 20 g. of hydrochloric acid in 60 c.c. of water. A saturated ferric chloride solution and the ferric chloride–hydrochloric acid solutions are erratic in their reaction with stainless steel, causing local pitting of the metal in some cases. In selecting an etching reagent, first consideration should be given to the ferric chloride, hydrochloric acid, and nitric acid mixture. A simple paraffin coating effectively protects the metal surface from acid. The methods of producing a black etch on steel and photographic etching are briefly described.—J. P. S.

Banded Structure in Steel. S. Baeckström. (*Jernkontorets Ann.*, 1952, **136,** Jan., 9–20). [In Swedish]. The literature on ' banded structure ' (or ' ghost lines ') is critically reviewed. Many theories have been put forward but none has been generally accepted. Investigations point to several factors combining to produce this phenomenon. Refining the solidification structure reduces the tendency to the formation of banded structure and to fibrous fracture. Proposed methods of refining are: (1) Low casting temperature; (2) small or chilled moulds; (3) low pouring rate; (4) superheating the steel in the furnace; and (5) special deoxidation processes. (39 references).—R. A. R.

X-Ray Line Broadening from Cold Worked Iron. J. H. Auld and R. I. Garrod. (*Nature*, 1952, **169,** Apr. 5, 579–580). From experiments in which the true integral line breadth was determined by a modification of Stokes' method, and Young's modulus taken as the mean of values calculated for constant stress and strain, it was concluded that iron lattice distortion, not particle size, is the predominant cause of line broadening.—A. G.

Ferrite Grain-Size Measurements for Ship-Plate Steel. J. E. Campbell, R. H. Frazier, and H. O. McIntire. (*Welding J.*, 1952, **31,** Feb., 78s–94s). Ferrite grain sizes were determined in Class A ship plate in the as-rolled condition and after austenitizing at various temperatures followed by cooling at different rates. Results obtained using intercept methods, grain counting, comparison with special series of photomicrographs, and a fracture method for rating the ferrite grain sizes, were compared. Grain counting was the most reliable method and was used to show the effects of austenitizing temperature and cooling rate on grain size.—U. E.

Brittle Fracture of Crystalline Materials as Surface Formation. M. Schreckenbach. (*Technik*, 1952, **7,** Feb., 65–73). Starting with Griffith's theory and Polanyi's energy considerations, and with reference to recent research into mosaic structure by Graf, the author formulates the equation $(\sigma_z^2/2E)(V/F) = \alpha/980{,}665$, where σ_z is tensile strength, E is the elastic modulus, α the free surface energy per unit area of the fracture surface, and V volume of mosaic blocks providing the surface energy of F the fracture surface. (60 references).—J. G. W.

The Causes and Mechanism of Chemical Non-Homogeneity of Alloys During Crystallization. V. M. Tageev. (*Doklady Akademii Nauk S.S.S.R.*, 1949, **67,** 3, 491–494). [In Russian]. An investigation of the causes and mechanism of the development of chemical heterogeneity during the crystallization of steel is described.—V. G.

X-Ray Methods of Testing. H. Stintzing. (*Feuerungstechnik*, 1942, **30,** May 15, 105–113). A review is first given of the field of X-ray techniques. This is followed by a description of sealed-off and continuously pumped X-ray tubes; particular emphasis is laid on the rotating anode type of tube. A description of the use of X-rays for the radiography of metal structures and opaque objects is followed by a description of counting tubes. The various crystallographic techniques for the determination of structures and particle size are described and illustrated by a table of results for different types of coke. Finally, the elements of X-ray spectroscopy are discussed.—R. J. W.

Fluorescent Screen as Aid in X-Ray Structure Examination. J. C. Lankes, Erika Orlamünder, and G. Wassermann. (*Z. Metallkunde*, 1951, **42,** Oct., 300–301). It was found that commercially available fluorescent X-ray screens facilitated the direct visual observation of interference spots from Bragg reflections of metal crystals in the rotating-crystal method and in the Laue method. The advantages of this direct observation over the conventional photographic procedure are discussed.—P. F.

Radiometallography. C. Chaussin. (*Mét. Constr. Méc.*, 1952, **84,** Jan., 35–37, 39; Feb., 99–101). The principles of production and the properties of X-rays are recorded. The requirements of good X-ray photographs are discussed. These include clarity of image, exposure, and elimination of secondary radiation. The main uses mentioned are: Weldments, castings, and assemblies. Finally, the nature of gamma rays, their production and their application in the examination of thicker parts are reviewed.—R. S.

The " Forging Cross " and Austenite Grain Size in Medium-Hard Carbon Steels. R. Mitsche. (*Berg- hüttenmänn. Monatsh.*, 1940, **88,** June, 77–80). From the cross-section of forged steel specimens (0·5% C and 0·4 to 0·6% Mn), the appearance of the austenitic grains in the form of a diagonal cross (the ' forging cross ') is described. The austenitic grain growth bears a certain relationship to the annealing, the specimens in the work described being annealed at temperatures from 800° to 1200° C. The cause of this is probably due to a change in the state of nucleation. A working hypothesis to explain the observed phenomena is given with micrographs clearly depicting the ' forging cross.'—R. J. W.

The ' Forging Cross ' and Austenite Grain Size in Unalloyed ' Under-Pearlitic ' and Pearlitic Carbon Steels. A. Legat and E. Plöckinger. (*Berg- hüttenmann. Monatsh.*, 1941, **89,** May, 53–58). The ' forging cross ' (*see* preceding abstract " The ' Forging Cross ' and Austenite Grain Size in Medium-Hard Carbon Steels " by R. Mitsche) appears with under-pearlitic steels due to the behaviour of the crystals in the strongly deformed zones. In the pearlitic steels no such striking marking is observed except under the microscope. The steels observed were made especially rich in nuclei and demonstrate these facts very clearly, as is shown by photomicrographs. After heat-treatment, a preferred grain growth occurs in these zones of heavy deformation, with a certain distribution of nuclei.—R. J. W.

Growth Spirals on Haematite (Fe_2O_3) Crystals. A. R. Verma. (*Nature*, 1952, **169,** Mar. 29, 540–541). From X-ray data the distance between successive layers of oxygen atoms is 2·3 Å. perpendicular to the (111) plane and the structure repeats itself every six layers, *i.e.*, at intervals of 1·4 Å. Observed growth spirals agree well with these facts.—A. G.

Can the Existence of the Gamma-Phase be Established in Iron Films Deposited from the Vapour Phase? H. König. (*Z. Metallkunde*, 1952, **43,** Jan., 26–28). Electron diffraction photographs obtained from thin iron films deposited from the vapour phase provide no evidence of the existence of the gamma-phase at room temperatures.—P. F.

Contribution to the Determination of the Critical Cooling Velocity of Steels. A. Legat and G. Unterhüber. (*Berg- hüttenmänn. Monatsh.*, 1940, **88,** July, 88–91). A graphical determination of the critical cooling velocity is given. Calculations were made on the mode of cooling of spheres and cylinders 20, 30, and 40 mm. in dia. and 60 mm. high, and a simple logarithmic standard was plotted. The speed of the austenitic transformation was known at different temperatures and, by plotting the cooling-velocity curves on the same graph, a graphical solution to the critical cooling speed was obtained.—R. J. W.

Some Considerations of the Problem of the Cooling and Over-Heating in the Transformation Phenomena of Steels. R. Mitsche and A. Legat. (*Berg- hüttenmänn. Monatsh.*, 1942, **90,** Dec., 187–189). The conception of ' overheating capacity ' of steels is distinguished as a non-equilibrium phenomenon. The effect of the overheating on the capacity for undercooling is discussed for the pearlitic transformation in steels. Finally, the effect of different alloying elements and the state of nucleation of the steel on the overheating capacity is described.

The Transformation of Austenite in Carbon Steels in the Pearlite Stage. R. Mitsche and A. Legat. (*Berg- hüttenmänn. Monatsh.*, 1942, **90,** Apr. 15, 43–47). In the decay of austenite in carbon steels at the pearlitic stage, the attractive influence of various nuclei is clarified. The original decay structure may be distinguished by lamellæ of high and low temperature pearlite, from direct austenitic decay, and from the agglomeration of the spherical form of cementite, respectively. The effect of annealing time on the process of dissolving the nuclei, and thus of the type of austenitic decay produced, is described in two series of experiments. The results are shown in 16 micrographs.—R. J. W.

Effect of the Austenitizing Temperature on the Ar Points of Structural Alloy Steels. A. Legat and E. Plöckinger. (*Berg- hüttenmänn. Monatsh.*, 1942, **90,** Nov., 169–175). A series of seven alloy steels was prepared in a basic-lined arc furnace.

It was shown that the onset of ferrite separation by cooling from the solid solution region was strongly affected by the initial temperature. In order to state the temperature from which one can cool from the solid solution region without the appearance of ferrite, reference to the previous treatment was essential. An increase in the initial temperature in the gamma region led, with the steels investigated, to an increase in the retention of hardness.—R. J. W.

The Question of Nuclei in Steels. R. Mitsche and A. Legat. (*Berg- hüttenmänn. Monatsh.*, 1939, **87,** Dec., 210–212). From basic considerations, it is shown that the occurrence of transformations in steels is considerably affected by the presence of nuclei, the effect varying with temperature. The austenitic and pearlitic, also the Ar_1, Ar_3, and Ac_3 transformations are considered. The nature of the nuclei, *e.g.*, non-metallic inclusions, carbides, or nitrides, also affects the texture.—R. J. W.

Carbide Phase During Tempering of Alloy Steels. S. Z. Bokshtein. (*Zhurnal Tekhnicheskoi Fiziki*, 1949, **19,** 5, 532–541). Changes in the composition and structure of ferrite and carbide phases in chromium steel during tempering were investigated.—V. G.

Law of Approach to Saturation for Martensite. N. S. Akulov and K. M. Bol'shova (*Doklady Akademii Nauk S.S.S.R.*, 1950, **71,** 4, 633–636). A study of the approach to saturation of a ferromagnetic crystal aggregate based on measurements of differential magnetic susceptibility is described. Non-equilibrium solid solutions in which large, markedly inhomogeneous, local stresses may exist, as well as heterogeneous alloys, were investigated.—V. G.

Reactions of Iron–Chromium Alloys with Oxygen. H. Wentrup and B. Knapp. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1941, **4,** July, No. 11, 237–256). The relationship between the affinity of oxygen for pure iron and additions of chromium was established by melting in a Tamman furnace and a high-frequency vacuum furnace. A useful contribution is made to the Fe–Cr–O ternary diagram. By comparison of the deoxidizing effect of various elements used for alloying with steel, chromium was found to be very similar to manganese. Finally, several suggestions are made for the recovery of chrome-rich slag in the preparation of ferro-chromium from chromium-bearing iron alloys.—R. J. W.

The Constitution of Iron–Nickel–Chromium Alloys at 550–800° C. A. J. Cook and B. R. Brown. (*J. Iron Steel Inst.*, 1952, **171,** Aug., 345–353). [This issue].

The Iron–Phosphorus–Antimony Phase Diagram. R. Vogel and D. Horstmann. (*Arch. Eisenhüttenwesen*, 1952, **23,** Mar.–Apr., 127–134). The equilibrium diagram for the Fe–P–Sb system has been derived. A second boiling point has been found in the P–Sb binary system; the two elements do not form any compounds with each other. A method has been worked out in which addition of copper permits the metallographic or chemical determination of the saturation value of phosphorus in molten antimony, which cannot be estimated by quenching methods. The complete Fe–P–Sb diagram, including the vapour phase, has been established and the conditions determined for a ternary second boiling point.—J. P.

Some Effects of Order–Disorder in Fe–Al Alloys. W. D. Bennett. *J. Iron Steel Inst.*, 1952, **171,** Aug., 372–380.) [This issue].

CORROSION

Oxidation, Corrosion and Wear of Metals and Alloys. J. Denax. (*Tecn. Indust.*, 1951, **29,** 1367–1370). [In Spanish]. This is a very general note on some forms of oxidation, corrosion, and wear, of ferrous and non-ferrous metals and alloys.

Mechanism of Oxygen Corrosion. R. Audubert. (*Compt. Rend.* 1952, **234,** Mar. 31, 1448–1450). By applying the theory of overvoltage to corrosion in the presence of oxygen, the mechanism may be determined from a comparison of experimental curves with various derived formulæ.—A. G.

Means and Methods for Corrosion Protection in the Light of the Technical and Patent Literature. R. Springer. (*Metalloberfläche*, 1951, **5,** Feb., A22–A28; Mar., A43–A46). Numerous patents and technical contributions from several countries, relating primarily to chemical methods of corrosion prevention and to processes for rendering exposed surfaces passive to attack, are listed and discussed. (113 references).—P. F.

On the Stress Corrosion of Austenitic Steels. H. J. Rocha. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1942, **5,** Jan., No. 1, 1–14). The practical conditions under which stress corrosion (crevice attack) may be observed are first described. The metallurgical basis of crevice attack and its correlation with austenite stability and carbon content are described by two series of experiments. The effect of texture on the corrosion is discussed under (*a*) the α–γ-mixed region, (*b*) steels containing cold-worked martensite, and (*c*) the effect of carbide precipitation in 18/8 Cr–Ni steels.—R. J. W.

Protecting Cold and Hot Water Installations Against Corrosion by Centralized Water Preparation. G. Seelmeyer. (*Gas u. Wasserfach*, 1943, **86,** Sept., 321–325). An investigation of the effect of 'magnofiltering' 26 different types of water on the corrosion properties and the tendency to deposit 'fur' is described. The formation and advancement of corrosion are considerably reduced in certain cold- and warm-water installations, and also to some extent in heating plant. The properties of the waters (*e.g.*, *p*H values) are clearly tabulated for (*a*) those in which corrosion was prevented, (*b*) those in which corrosion was light, and (*c*) those unaffected by the filtering process.—R. J. W.

Corrosion History of a Domestic Hot Water System. J. R. Baylis. (*J. Amer. Water Works Assoc.*, 1952, **44,** Mar., 224–238). The condition of a galvanized-iron hot-water tank after 22 years is described. Long finger-like rust tubercles were found inside the tank; they are considered to have grown downwards. Pits with covering tubercles appeared to form in the same general manner in hot as in cold water. A gas heater with copper coils showed no corrosion. A furnace heater made of black iron pipe failed after 21 years owing to corrosion from the outside; a layer of $CaCO_3$ was found on the inside. Boilers with straight copper tubes corrode badly unless protected by a layer of $CaCO_3$.—B. G. B.

Speed and Mechanism of Corrosion of Iron—Influence of *p*H, Chlorides and Chromates. M. Pourbaix. (*Soc. Roy. Belge. Ing., Mém.*, 1951, Nov., 71–76). Experiments have been carried out on the corrosion of iron by aqueous solutions exposed to air. In the absence of chloride, caustic soda gives complete passivation for *p*H values above 10·3; for a *p*H less than 10·0 corrosion becomes general. Addition of chloride raises the *p*H necessary for passivation to about 12·6, and general corrosion occurs below a *p*H of 10·3. It is important to note that corrosion becomes local between *p*H 10·3 and 12·6. The addition of chromate causes local corrosion or gives complete passivation depending on the *p*H of the solution and the chloride content. Addition of $NaHCO_3$ or Na_2CO_3 enables the chromate concentration to be reduced without affecting the protective properties of the solution.

B. G. B.

Rust- and Acid-Resisting Steels For Chemical Engineering. H. Braun. (*Werkstoffe u. Korrosion*, 1952, **3,** Mar., 93–98). The author gives a short practical survey of the factors governing the successful and economical use of rust-resisting steels in chemical engineering. It is vital that the composition of the steel shall be appropriate for its particular conditions of service, but it is by no means always necessary to use the most highly alloyed steels; *e.g.*, for certain applications, economies can be made by using 17% Cr steel instead of austenitic Cr–Ni–Mo steels. Full advantage should be taken of the reduction in plate thickness rendered possible by the superior corrosion resistance of the rust-resisting steels, mechanical strength being secured when needed by external reinforcements of cheaper materials. Various corrosion problems are discussed. Most of them result from the use of steels of unsuitable composition or faulty technique in fabrication. Perfect cleanliness of both the inner and outer surfaces of apparatus is essential, because contact with dust, millscale, or rust from external sources causes breakdown of rust-resisting steels.—J. C. H.

Some Factors Affecting the Resistance of Austenitic Cr–Ni Steels to Attack by Hot Concentrated Nitric Acid. H. T. Shirley and J. E. Truman. (*J. Iron Steel Inst.*, 1952, **171,** Aug., 354, 358). [This issue].

Rust. M. Ragg. (*Werkstoffe u. Korrosion*, 1952, **3,** Mar., 102–105). A general discussion of the economic importance and mechanism of rusting and of the effects of differences in climatic conditions on the rate of atmospheric corrosion of mild steel is presented.—J. C. H.

Hydrogen Sulphide Corrosion Cracking of Steel. L. W. Vollmer. (*Canad. Min. Met. Bull.*, 1952, **45,** Feb., 103–109) Two unexpected failures in 9% nickel steel tubing, used in a well drilled in the sour condensate Pincher Creek field of south-west Alberta, after only six days' service in production

tests, instigated an extensive investigation into the behaviour of steels in H_2S environments in general, and in sour condensate wells in particular. Initial results are presented. Susceptibility to failure is not limited to 9% nickel steels, but most steels heat-treated to Rockwell hardness C24 or above may be susceptible to the failure process. Plastic deformation increases the susceptibility. Embrittlement by exposure to H_2S is not considered a primary cause of failure, but it may be a contributory factor. There is evidence that a metallographic structural phase as a network may be the sensitizing factor.—T. E. D.

New Way to Detect and Locate Corrosion. J. B. McAndrew, W. H. Colner, and H. T. Francis. (*Chem. Eng.*, 1952, **59,** Feb., 305–309). An outline is given of the detection and location of corrosion, utilizing the A.C. signal produced from anodic and cathodic areas when the specimen is rotated. The D.C. potential is readily blocked by a series capacitance. The specimen is rotated at 1725 r.p.m.—T. E. D.

Preventive Measures against Corrosion. A. Marsden. (*Gas World*, 1952, **135,** Mar. 29, 314–317). Conditions causing corrosion in the atmosphere, underground, under water, and in steam systems are discussed. Protection by metallic and non-metallic surface films and paints, with details of their correct use, are mentioned.—T. E. D.

The Inspection and Care of Gas Holders. D. P. Dalby. (*Gas World*, 1952, **135,** Mar. 29, 323–325). Lubrication of guide wheels by Stauffer lubricators is recommended. Some improvements in holder design, to assist in the prevention of corrosion, are suggested.—T. E. D.

Pit or Cavity Corrosion of High Chromium Stainless Iron Caused by Contact with Non-Conductive Substances, and Its Prevention. A. Endo. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1949, **1,** Dec., 349–356). [In English]. When the surface of a 21–35% Cr stainless iron comes into contact with insulators such as glass, cork, or with noble metals, a narrow crevice acting like a capillary is formed, and corrosion takes place in the pit or cavity at the point of contact. The author finds that an addition of 7% molybdenum to a 22% Cr iron and quenching in water suppresses the corrosion. The mechanism of the process is discussed.—J. G. W.

How Austenitic Nickel Cast Iron Can Serve as an Alternate for Caustic Manufacture. H. O. Teeple. (*Chem. Eng.*, 1951, **58,** Dec., 286). Ni-Resist, Type 3, a 30% nickel–iron, is resistant to thermal shock, and its corrosion rate in boiling 50–65% NaOH is 0·0004 in./year.—T. E. D.

Intergranular Corrosion of Stainless Chromium–Nickel Steels. J. Hochmann. (*Étude Document Mét.*, 1951, Oct.–Dec., Bull., 115–134). Methods of studying intergranular corrosion are described, including one using the change in electrical resistance of the specimen. Theories on the causes of this corrosion in austenitic steels are discussed, and means of diminishing sensitivity to corrosion are suggested.—T. E. D.

Some Aspects of Ship Bottom Corrosion. P. Ffield. (Soc. Naval Architects and Marine Engineers: *Corrosion*, 1952, **8,** Jan., 29–48; Feb., 69–88). Bottom corrosion is not a problem of general wastage, but of local pitting at higher rates of corrosion. Pitting is basically an electrochemical effect, the loss of metal occurring whenever electric currents flow from the metal to the sea water. The two most vigorous forms of hull corrosion due to pitting arise either from stray electric currents returning to a shore source or from galvanic currents flowing between dissimilar metals and, in particular, between base steel and mill-scale. Factors which can influence the extent of mill-scale corrosion include (*a*) rolling-mill practice as it affects the composition of the scale, (*b*) duration of weathering, (*c*) type of bottom composition, and (*d*) adequate maintenance of bottom painting. Complete removal of mill-scale by pickling or sand-blasting is the safest remedy, followed by surface painting as soon as possible.—G. P. A.

The Chemical Resistance of Phenolic and Furfuryl Alcohol Type Coatings. R. B. Seymour and R. H. Steiner. (*Corrosion*, 1952, **8,** Feb., 65–68).—G. P. A.

Bacterial Corrosion of Construction Materials. C. D. Parker. (*Commonwealth Eng.*, 1951, **39.** Dec., 190–196). The author defines bacterial corrosion as the destruction of a material of construction by chemical processes brought about by the activity of a specific type or types of bacteria developing in the environment adjacent to the material concerned. Among the materials subject to bacterial corrosion are cast iron, wrought iron, steel, brass, and concrete. The agents responsible for the corrosion of these materials are discussed. The diagnosis, prediction, prevention, and cure of this type of corrosion are described.—J. P. S.

The Salt-Spray Test. (*Metal Ind.*, 1952, **80,** Feb. 15, 123–126). The salt-spray test, which is largely used as an accelerated corrosion test, is described. Its limitations and disadvantages are discussed, and the necessity of carefully standardized conditions as specified by the A.S.T.M. is emphasized. The test has many applications, the following being described: porosity testing of cathodic coatings, checking thickness of anodic coatings, estimating life of metallic coatings, testing organic and conversion coatings, and studying galvanic corrosion between pairs of metals.—P. M. C.

Research on Corrosion Tests in Salt Sprays. G. Bianchi and A. Mora. (*Met. Ital.*, 1952, **44,** Jan., 9–13). The operation of a salt-spray chamber for corrosion tests is described. The characteristics of fogs are determined by sedimentation tests and by a new method using solarized photographic plates. Dimensions of fog particles are determined.—M. D. J. B.

Effectiveness of Cathodic Currents in Reducing Crevice Corrosion and Pitting of Several Materials in Sea Water. T. P. May and H. A. Humble. (*Corrosion*, 1952, **8,** Feb., 50–56). Crevice corrosion and pitting occur when chromium-bearing and chromium–nickel stainless steels are immersed in quiet sea water. The crevice corrosion is of the oxygen concentration cell type of attack. Tests conducted at Kure Beach, N.C., have shown cathodic protection to be useful in preventing crevice corrosion and pitting on chromium–nickel steels when immersed in quiet sea water. The chromium-bearing steels cannot be completely protected cathodically owing to severe blistering when the current is sufficient to eliminate the corrosion. This blistering is due to hydrogen produced at cathode surfaces. Hydrogen is also generated on mild-steel surfaces but does not ordinarily produce blistering.—G. P. A.

Corrosion of Thin Wires I, Corrosion of Thin Wires of German Silver, Eureka, Copper and Iron by Sea Water. H. Yoshisaki. (*Sci. Rep. Res. Inst. Tôhoku Univ.*, A, 1950, **2,** Feb., 96–101). [In English]. Experiments verified the expectation of the singular behaviour of thin wires, which corrode slowly at the surface but quickly in the core. The cause of this is the inhomogeneous distribution of chemically active points.—J. G. W.

Extraneous Currents Noted on Large Transmission Pipe Line System. N. J. Allison and W. E. Huddleston. (*Corrosion*, 1952, **8,** Jan., 1). This reports briefly the observation, on a 1128-mile long, large diameter pipeline, of a stray current not attributable to any of the usual sources. Cathodic protection still facilitated complete protection.—G. P. A.

On the Inhibitor for the Corrosion by Hydrochloric Acid on High-Chromium Steels. H. Endo and S. Isihara. (*Sci. Rep. Res. Inst. Tôkohu Univ.*, A, 1950, **2,** Apr., 209–215). [In English]. The action of potassium dichromate as the inhibitor of the corrosion of high-chromium steels by HCl was investigated. The smallest amount of potassium dichromate for complete passivation was proportional to the square of chromium content, and was greatly reduced by the presence of molybdenum in solid solution in the steel, but reduced much less by tungsten.—J. G. W.

What Must Be Known and Done before Reaching a Decision on Laying a New Pipeline. A. J. Maurin. (*Ind. Pétrole*, 1951, Apr.). The choice of route is often a compromise between the shortest path and government regulations. Certain types of soil having an abnormal *p*H or high concentration of chloride ion should be avoided if possible. Notes are given on the calculation of the diameter of the pipe required for liquids or gases. The geophysical and geo-electrical investigations that must be carried out are described. Finally, the economics of 12 different methods of protection are discussed.—B. G. B.

The Anticorrosive Protection of Underground Conduits and the Prospecting of the Soil. A. J. Maurin. (*Congrès du Pétrole, La Haye*, 1951, Section 8, Preprint 5). Geophysical prospecting in the proposed direction of a new pipeline enables the protection to be determined in advance. The application and regulation of cathodic protection devices are discussed. The use of the Fe–H_2O equilibrium diagram and composite graphs of thermodynamic properties are explained. Galvanic protection, using magnesium anodes, and five different methods of electrical protection are described.—B. G. B.

Ten Years Study of the Corrosion of Underground Conduits. A. J. Maurin. (*Congrès Assoc. Tech. Gaz.*, 1949). The author

shows how the Fe–H_2O equilibrium diagram can assist in the study of corrosion problems. The application of the thermodynamic theories of Pourbaix and the importance of *p*H, potential, and soil resistivity are explained with diagrams. A review is made of the available methods of measuring the *p*H, potential, and resistivity of the soil.—B. G. B.

ANALYSIS

Micro-Analytical Test Methods for Investigating Iron and Steel. P. Klinger, W. Koch, and G. Blaschczyk. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1940, **3**, Nov., 255–273). In this very comprehensive article quantitative methods of micro-analysis for carbon, iron, silicon, manganese, phosphorus, sulphur, aluminium, nitrogen, chromium, nickel, molybdenum, tungsten, titanium, and vanadium are outlined. In the final paragraph, the various methods of separation of these elements are given ; *i.e.*, (1) ether separation, (2) electrolytic separation, (3) by direct decomposition of the carbonate, and (4) by separation from ammoniacal salts.—R. J. W.

Quantitative Analysis of Molybdenum in Steels. A. Calderon Lambas. (*Inst. Hierro Acero*, 1951, **4**, Oct.–Dec., 315–317). [In Spanish]. The adaptation of the optical method of F. de Ibarra to the photocell for the quantitative evaluation of molybdenum in steel, is examined. It is considered to be an ideal method as regards rapidity and precision. Cobalt and vanadium must first be removed, but tungsten makes practically no difference.—R. S.

Determination of Magnesium in Cast Irons. I—Spectrographic Method. R. Paton. **II—Chemical Method.** J. Fuchs. (*Fonderie*, 1951, Aug.–Sept., 2605–2612). A Jobin-Yvon medium-dispersion spectrograph was used. The author describes the preparation of the specimens, selection of rays, conditions of excitation, and details of aperture, filter, exposure, and treatment of the photographic plate. The method is simple and accurate but takes 2 hr. The following operations in the chemical method are described: (1) Separation of iron by electrolysis: (2) separation of manganese by ammonia; (3) separation of calcium by ammonium oxalate; (4) precipitation of ammoniacal magnesium phosphate; (5) determination of magnesium by gravimetric or volumetric method.—R. S.

Determination of Chromium and Vanadium by Potentiometric Titration. P. Enghag. (*Jernkontorets Ann.*, 1951, **135**, Dec., 621–634). [In Swedish]. A titration method is described. Dichromate and vanadate are reduced in the usual way by ferrous ammonium sulphate, the reduction being followed potentiometrically. The use of the Pt–W electrode pair has some advantages over the Pt–calomel pair formerly used. If chromium and vanadium are both present, the first titration gives the sum; the vanadium is determined with the same ferrous ammonium sulphate after oxidation of the cold solution with permanganate, reduction of the excess with potassium nitrite, and the addition of urea.—R. A. R.

Spectrophotometric Determination of Silicon in the Presence of Zirconium, Beryllium, Aluminium, and Calcium. A. B. Carlson and C. V. Banks. (*Analy. Chem.*, 1952, **24**, Mar., 472–477). The molybdenum blue method, in conjunction with hydrofluoric acid treatment of the samples, is described fully, with particular reference to its use in the presence of zirconium, beryllium, aluminium, and calcium. Results indicate a close relationship between *p*H, fluoride concentration, and rate of formation of molybdisilicic acid. Reduction to heteropoly blue complex is fairly free from interferences.

Oxygen Analyses. R. S. Medlock. (*Instrument Engineer*, 1952, **1**, Apr., 3–10). An instrument is described which continuously measures the magnetic susceptibility of a gas mixture and provides a continuous record and automatic control of oxygen concentration. A theoretical analysis enables a useful prediction to be made of the influence of variables other than oxygen concentration on the accuracy of measurement.—J. P. S.

Rapid Analysis Determines Cerium in Steel. C. M. Johnson. (*Iron Age*, 1952, **169**, Jan. 17, 94–96). A rapid method of determining the cerium group rare earth content in steels where they are used as additive agents is described. The method involves precipitation with dry sodium peroxide powder from the still acid sulphate solution. Lanthanum and neodymium are also precipitated with the cerium.

Photometric Determination of Copper in Iron and Steel with Diethyldithiocarbamate. J. L. Hague, E. D. Brown, and H. A. Bright. (*J. Res. Nat. Bur. Stand.*, 1951, **47**, Nov., 380–384). A method is described for the direct photometric determination of copper in steel and iron. The sample (0·1–0·25 g.) is dissolved in diluted nitric acid, and a sulphuric–phosphoric–perchloric acid mixture is added. The solution is evaporated to fumes of sulphuric acid, diluted, and the sodium salt of dimethylglyoxime or ethylenediaminetetra-acetic acid added as a complexing reagent. The copper diethyldithiocarbamate is then formed and extracted with butyl acetate. The butyl acetate extract is washed with diluted sulphuric acid and the absorbency of the copper complex is measured at 560 to 600 mμ. The result is accurate within ± 0·005% for steels containing 0·05–0 ·25% of copper.—J. P. S.

Determination of Manganese in Iron and Steel with Red Lead. M. V. Kharitonova. (*Zavodskaya Laboratoriya*, **16**, 1950, 7, 876–877). The use of red lead instead of lead peroxide for the volumetric determination of manganese in ferrous alloys is described.—V. G.

Polarography with Alternating Currents. IV—A.C. Polarography of Uranium, Iron, Nickel, and Manganese. B. Breyer, and S. Hacobian. (*Australian J. Sci. Res.*, 1951, **4**, Dec., 604–609). The A.C. polarography of uranium, iron, nickel, and manganese in suitable supporting electrolytes is discussed. Uranium was estimated in perchloric acid as the uranyl ion (UO_2^{++}); iron as the oxalcito complex ion in neutral or acid oxalate. Nickel and manganese were estimated as cyano complexes which are reversibly reduced at the dropping mercury electrode.—J. P. S.

Polarographic Methods in the Iron and Steel Industry. I. Principles and Applications of Polarography. II. Principles and Applications of Amperometric Volume Measurement. F. Burriel Marti and F. Lucena Conde. (*Inst. Hierro Acero*, 1951, **4**, Apr.–June, 137–142; Oct.–Dec., 318–322). [In Spanish]. The principles of polarographic analysis, including the analysis of polarographic waves, closed and open cells, and methods of procedure are surveyed. Examples are given of the determination of Ni, Pb, and Cr. The principles of amperometric methods, which may be considered as a derivation of polarography, are stated. The electrolyte consists of a concentrated base solution of a salt whose cation has a fairly high decomposition potential, and the solution to be analysed, usually diluted. It is possible to measure: (1) The quantity of the reactant which, on reaction with an ion or given compound electro-active to the fixed potential, is necessary to eliminate its polarographic wave; (2) the quantity of the electro-active reactant required to react with an ion or compound which produces no wave. In this case the result is determined by the point at which the reactant begins to produce a diffusion current. Experimental details are given. R. S.

Reliability of Photoelectric Photometry. N. T. Gridgeman. (*Analy. Chem.*, 1952, **24**, Mar., 445–449). The theory of the precision of the commoner instruments, as influenced by the concentration of the measured solution, is developed to yield a general expression, of which all valid expressions in the literature are shown to be special cases. Transmittance of 30 to 50% is considered to be the optimum range. The precision of the transmittance-ratio technique is interpreted in the light of the general theory of observational errors.—T. E. D.

The Possibility of Applying Hollow Cathode Discharges for Spectrum Analysis Investigations. H. Schüler. (*G.A.M.S. Colloque International de Spectrographie*, Oct. 12–14, 1950, 169–171). The properties of the cooled hollow cathode are discussed, and it is pointed out that such discharges are also useful, under proper conditions, for quantitative spectrographic analysis. By reduction of the oxides on the hollow cathode surface it is possible to analyse samples of any desired composition.

Direct Gravimetric Determination of Moisture in Coal. H. W. Deinum and M. L. Goedkoop. (*Chemisch Weekblad*, 1952, **48**, Mar. 22, 170–173). [In Dutch]. The hygroscopic properties of coal and its readiness to react with oxygen limit the application of the indirect determination of its moisture content to the technical analysis. For coal research and elementary analysis the determination of the moisture content by heating and weighing the residue (oven drying) is not applicable. It is proposed to expel the moisture by means of dry oxygen-free nitrogen at 105° C. and to collect it in a tube of known weight containing anhydrone, after which the expelled water is weighed directly.

Problem of the Determination of Tar and Oil Mists in Coke Oven Gas and the Determination of Small Contents of Moisture.

K. Scheeben. (*Technische Mitteilungen Krupp, Forschungsberichte*, 1942, **5**, Jan., 18–22). The determination of the tar-oil mist content in coke-oven gases and that of the accumulative errors are simply described. In connection with this analytical investigation an ancillary apparatus was developed for the determination of small quantities of water. Experimental results substantiate the usefulness of the method.—R. J. W.

Determination of Phenols in Aqueous Wastes from Coke Plants. J. A. Shaw. (*Analy. Chem.*, 1951, **23**, Dec., 1788–1792). The method described here is a combination of the bromine turbidimetric method and a procedure using 4-aminoantipyrine and potassium ferricyanide, carried out under rigidly controlled *p*H conditions. The delicacy of the method is about 20 parts per 10°, and a determination can be made in from 30 min. to 2 hr., depending on the amount of phenol in the sample and the concentration required.—T. E. D.

The Determination of Moisture in Coal Using the Karl Fischer Reagent. A. Bryson and W. F. Pickering. (*J. Inst. Fuel*, 1952, **25**, Jan., 28–30). This paper describes the successful application of a direct Karl Fischer reagent titration to the estimation of moisture in bituminous coals, using a ' dead stop ' end-point.—J. P. S.

The Sampling of Lump Solid Materials by the Method of Random Selection. A. Palazzi. (*Rev. Mét.*, 1952, **49**, Jan., 22–34). Nomograms are given, enabling the weight of sample, number of portions per sample, size to which sample should be reduced, and accuracy of results to be determined.—A. G.

Coal Sampling. F. D. K. Liddell. (*Fuel*, 1951, **30**, Dec., 275–283). The literature on coal sampling is examined, and the general principles on which a sampling specification should be based are discussed. The ideal specification should be flexible and should provide a self-contained estimate of its accuracy in any particular case. These requirements can be met by sampling in duplicate and using standard statistical techniques.—J. P. S.

Determination of Phosphorus in Coal. F. Ellington and W. N. Adams. (*Fuel*, 1951, **30**, Dec., 272–274). A method for the determination of phosphorus in coal and coke is proposed, in which a solution of the inorganic constituents of the coal is obtained by wet oxidation, a calorimetric method being applied to the solution for the determination.—J. P. S.

Valve *p*H Meter. L. I. Belen'kii and Ya. B. Rozman. (*Zavodskaya Laboratoriya*, 1950, No. 1, 120–123). [In Russian]. A robust *p*H meter with screened glass electrodes is described, which is designed to work directly from the normal industrial circuit. The instrument works at temperatures up to 45–50° C.—S. K.

Sorting Tungsten Steel from Carbon Steel Scrap. (*Engineering*, 1952, **173**, Mar. 28, 416; *Machine Shop Magazine*, 1952, **13**, Apr., 164–165). **Sorting Scrap.** (*Aircraft Prod.*, 1952, **14**, May, 153). Tungsten steels are to a large extent resistant to rusting, and this resistance is markedly superior to that of carbon steels. A simple accelerated rusting test, using ammonium chloride solution, is described for distinguishing between the two steels.—T. E. D.

Spectrochemical Analysis of Refractories. G. Hartleif and H. Kornfeld. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 103–105). A rapid spectrochemical method has been developed for the determination of Al_2O_3, TiO_2, Fe_2O_3, CaO, and MgO in quartzite and crude silica. The ground sample is mixed with ammonium chloride and strontia, and filled into a central cavity in the lower carbon electrode. The strontia serves to regulate the temperature of the exciting spark. The time for analysis is about 30 min. as against the 2–3 days for ordinary chemical methods with which its accuracy compares very favourably.—J. P.

Determination of Iron in Ores, Slags, and Refractories. Methods of Analysis Committee. (*J. Iron Steel Inst.*, 1952, **171**, Aug., 401–412). [This issue].

The Spectrographic Analysis of Slag and Ore. C. G. Carlsson. (*Jernkontorets Ann.*, 1951, **135**, Dec., 607–620). [In Swedish]. The spectrochemical method of the author and J. T. M. Yü (*see J. Iron Steel Inst.*, 1950, **166**, 273–280) for analysing steelmaking slags has been modified for the determination of rock constituents of iron ore concentrates. It was necessary to incorporate a fluxing operation in order to convert all samples to the same mineralogical state. The best of several procedures was to mix 200 mg. ore (— 100 mesh) with 1600 mg. powdered $Na_2B_4O_7$ and to melt this for 3–4 min. on a large platinum lid from which the thin cake was easily removed. The fused cake was pulverized and 400 mg. of the powder mixed with 300 mg. graphite powder and pressed into a cake and analysed in the same way as slag, except that the primary resistance was raised from 70 to 120 ohms. Iron was used as the reference element.—R. A. R.

Rapid Spectrochemical Analysis of Metallurgical Slags. G. Hartlief and H. Kornfeld. (*Arch. Eisenhüttenwesen*, 1952, **23**, Mar.–Apr., 107–111). A rapid spectrographic method has been worked out for determining calcium, iron, manganese, magnesium, aluminium, titanium, vanadium, and silicon in steelmaking and blast-furnace slags. The ground sample is fused with borax, dissolved in an aqueous citric-acid/sodium-citrate solution and a portion of the solution, placed on the flat ends of carbon electrodes and sparked without external standards. The accuracy for low and medium concentrations is about $\pm$ 5%; for high concentrations it is much smaller. An examination of a sample takes about 2 hr.—J. P.

Using Acetic Anhydride in the Estimation of Silica. J. Lamure and Henriet. (*Chim. Analy.*, 1952, **34**, Apr., 88). The use of acetic anhydride for the more rapid dehydration of silica in slag analysis is described, and the accuracy is compared with that of two other methods.—T. E. D.

The Determination of Ankerite in Spathic Iron Ore. H. Kirchberg. (*Berg- hüttenmänn. Monatsh.*, 1940, **88**, June, 73–77). Ankerite often appears in a matrix of rocky spathic iron ore and in most cases is very difficult to determine. A new method has therefore been developed in which a surface of the rock was etched with an aqueous solution of hydrofluoric acid, coloured with ammonium sulphide, and treated afterwards with $CuSO_4$ solution. The ankerite appears grey to jet black whilst the spathic iron ore and rocky matter remain unaffected.—R. J. W.

ECONOMICS AND STATISTICS

Mining and Metallurgical Industry of Vizcaya. L. Barreiro Zabala. (*Met. y Elect.*, 1951, **15**, Dec., 72–73). [In Spanish]. The author traces the development of the Somorrostro region. Statistics are given of iron ore, pig iron, and steel production in Vizcaya from 1890 to 1950.—R. S.

Non-Ferrous Metals and Ferro-Alloys, Statistics 1951. (*Azienda Mineralii Metalliaci Italiani*, 1951). This book contains 159 pages of tables and data on the production, foreign trade, prices, and consumption, for Italy and the principal producing countries, of non-ferrous ores, metals, and ferro-alloys.—R. A. R.

Steel Production and Consumption Trends in Europe and the World. (*Steel Section, Economic Commission for Europe*, Apr., 1952, United Nations Department of Economic Affairs).

Growth of Alloy Steel Industry in India. K. N. Srivastava and P. K. Gupta. (Indian Institute of Metals: *Metal Market Review*, 1952, **5**, Apr. 14, 17–19; Apr. 21, 13–16).

MISCELLANEOUS

Organization of Research. E. Sörensen. (*Z. V.d.I.*, 1952, **94**, Feb. 21, 158–160). This is a summary of the International Symposium on the Organisation of Scientific and Industrial Research, which took place in London in November, 1951.—J. G. W.

The British Cast Iron Research Association, J. G. Pearce. (*Giesserei*, 1951, **38**, Dec. 28, 664–667). The author explains the organization and scope of activities of B.C.I.R.A. and its position relative to university and industry. Past achievement and current programmes are described.—J. G. W.

Technical Progress through Co-operation of Research Institutes with the Industry. K. Gierdziejewski. (*Przeglad Odlewnictwa*, 1952, **2**, 1, 4–6). [In Polish].

The Definition of Some Terms in Current Use in Metallurgy. H. Godfroid. (*Usine Nouvelle*, 1952, **8**, Jan. 31, 49–51; Feb. 7, 47–49; Feb. 14, 47–49; Feb. 21, 47–49). About 250 terms commonly used in metallurgy are accurately defined and arranged in alphabetical order.—T. E. D.

Units and Dimensions—Some Notes on the M.K.S. and C.G.S. Systems. J. B. Laurie. (*Elect. Rev.*, 1952, **150**, Jan. 11, 60–62). The introduction of a fourth dimension to the M.K.S. system of units and L.M.T. system of dimensions is discussed. A table of dimensions and units of the principal electromagnetic concepts is shown, taking $[Q]$ as the fourth fundamental dimension and retaining $\mu_0 = 10^{-7}$ for units of electromagnetic quantities. The ' inter-systemal ' conversion is described where 4π is credited with a dimension.—H. D. W.

Automatic Control in Industry. A. Justin. (*Research*, 1952, **5**, Jan., 11–15). This is an introduction to a series of articles, to appear later, reviewing the possible applications of automatic control in several different industries. It reviews, in simple terms, recent developments in automatic control, and the general principles that govern what can and cannct be done.—C. J. B. F.

Maintenance of Building Structures. R. O. Chapman. (*Iron Steel Eng.*, 1951, **28**, Dec., 85–88). A description is given of a maintenance scheme for structures in iron and steel works. The defects are reported on standard maintenance forms and classified into three groups: (1) Work which requires immediate attention; (2) work of lesser urgency; and (3) work which can be deferred to suitable maintenance periods. Information is given on the maintenance of crane runways, painting and protective coatings, roof repairs, brick buildings, and skylights.—M. D. J. B.

Colour in the Works and the Laboratory. E. Saffre. (*Peint. Pig. Vern.*, 1952, **28**, Apr., 231–241). The physical properties of colour are discussed, and colorimetric analytical methods are mentioned. The psychological effects of colour in the interior decoration of offices, laboratories, and works are considered, and examples are given.—T. E. D.

Codes for Describing Steel. F. P. Fischer. (*Technische Mitteilungen Krupp, Technische Berichte*, 1940, **8**, Dec. 5, 83–89). From a short historical survey, proposals are made for the code markings of unalloyed steels and steels containing up to 5% of an alloying element. The proposals for the unalloyed steels are obtained directly from ISA17, whilst for the alloy steels, the percentage content of the different elements is multiplied by various factors. For example, for a steel containing 0·15% carbon, 1% chromium, and 0·2% Mo, the code marking proposed is 15CrMo42 (the carbon content × 100, the chromium content × 4 and the molybdenum × 10). Proposed code markings for a variety of steels are tabulated against the chemical compositions.—R. J. W.

Concerning a Pyrophoric Iron Oxide. F. Lihl. (*Monatshefte für Chemie*, 1950, **81**, May, 632–846). A study of the structures of iron oxides obtained by thermal decomposition of ferrous formate and ferrous oxalate is described, and their pyrophoric properties are explained.—V. G.

Education and Training in Industry. G. R. Bashforth. (*Brit. Steelmaker*, 1952, **18**, Feb., 70–78). In addition to discussing the wider aspects of training for industry, the author considers the special requirements of junior operatives, craft apprentices, clerks, and technical apprentices. Suggestions are made on methods of adult education, and a final section is devoted to the training of foremen.—G. F.

The Industrial Relations Responsibilities of a Supervisor. O. U. Walker. (Eastern States Blast Furnace and Coke Oven Assoc.: *Blast Furn Steel Plant*, 1952, **40**, Mar., 318–322). The author discusses the supervisor's task in sustaining the morale of the works personnel.—J. P. S.

Wood Screws Now Being Manufactured at USCO. (*USCO Mag.*, 1952, **3**, Mar., 7–11, 21). A short description is given of the new factory of the United Steel Corporation of South Africa, which commenced operation in Nov. 1951, for producing woodscrews in steel and brass, metal thread screws, and rivets.—B. G. B.

Automatic Dust Sampler: A Self-Contained Unit. H. Lloyd, G. E. Winder, and D. A. Gillard. (*Iron Coal Trades Rev.*, 1952, **164**, Jan. 18, 149–151). A description is given of the construction and operation of a self-contained automatic dust-sampling unit, developed at the Safety in Mines Research Establishment. Provision is made for four stain samples per hour to be taken on a continuous strip of filter paper, the stains being rapidly evaluated by a densitometric method.

BOOK NOTICES

ASTBURY, N. F. "*Industrial Magnetic Testing.*" Physics in Industry Series. La. 8vo., pp. 132. Illustrated. London, 1952: Institute of Physics. (Price 25*s*.)

That this book is over-analytical in parts, whilst in others it is but a compilation—a criticism accepted by the author in his preface—is indeed an indication of its usefulness, since it is in the analytical approach that its merit largely lies. In so far as it consists of a compilation it has the advantage that the treatment is not merely descriptive, but is accompanied by comment from an expert in the field.

It is in the first three chapters dealing with general concepts, the magnetic circuit, and instruments, that the mathematical analysis is perhaps most valuable. It is essential, however, to realize the limitations of a treatment that to a certain extent must be approximate, and these limitations are, in general, clearly stated. Stress is also laid on the limitations of the experimental measurements that can be made on a magnetic circuit and also on the correct interpretation of these measurements.

It is to be regretted that the development of the mathematical analysis is unduly hurried in places. The effort required from the reader in following successive steps in the text might occasionally have been reduced by further simplification without transforming the book into a purely mathematical treatise. The alternative for the reader is to accept the development without a clear understanding of what is involved—a safe but somewhat unsatisfying process.

In particular, in Chapter 2, Section 2.2, in the discussion of the relationship between the values of induction and field in an annular ring which are experimentally accessible, the reader may be confused because of the lack of a clear statement that the equations developed apply only to a ring of rectangular cross-section. A statement of this limitation is again omitted when reference to these equations is made in Chapter 4.

Chapters 4 and 5 deal very satisfactorily with permeability and power-loss measurements, respectively.

Perhaps of greater value is Chapter 6, dealing with alternating-current bridge methods of testing, the treatment being as comprehensive as may be in a book of this size. Particular emphasis is given, where it is perhaps most needed, to the interpretation of the results of bridge measurements.

The testing of permanent magnets is described in Chapter 7, which deals also with the general problem of gap flux measurements. Reference is made to the new approach using nuclear resonance, which reveals the existence of a natural 'absolute' unit of field strength.

Appendices to the book include a tabulation of general magnetic properties of a range of hard and soft materials, provided as a guide to orders of magnitude.

Professor Astbury has produced, within this relatively small book, a work of great interest to all concerned with technical magnetic measurements and their physical basis.

A. P. H. JENNINGS

ATKINS, E. ARTHUR, and A. G. WALKER. "*Electric Arc and Oxy-Acetylene Welding.*" A Practical Handbook for Works Managers, Welding Operators, and Students. Fourth edition, revised by W. A. Atkins and A. G. Walker. 8vo, pp. xi + 352. Illustrated. London, 1952: Sir Isaac Pitman and Sons, Ltd. (Price 30*s*.)

This is the fourth edition of a book which was, no doubt, something of a classic when first published 30 years ago. It was written to serve the practical needs of works managers, welding operators, and students.

It is claimed that the previous edition, which appeared in 1936, has been considerably amended to bring it up to date. Success has not been achieved in this aim, and the general impression created is that of antiquity; too much of the original material has been left in, and not enough of the more recent developments in welding have been added.

The subject matter covers principally metallic-arc welding and oxy-acetylene welding, brief reference being made here and there to other processes. In the first chapter, confusion arises as to what is meant by flash welding, cross-wire welding, and contact welding. Flash and contact welding are first grouped together as one process, and, later, contact welding is described as a process for the manufacture of wire mesh, a process now known as cross-wire welding.

Furnace brazing in a controlled atmosphere is referred to as "Hyding or Copper Welding" and it is stated that this method has interesting possibilities, but it is difficult to say what may be the result of this method. Such a view is obviously many years out of date, furnace brazing now being a most important process in present-day production.

Throughout the book, one is constantly reminded of its original date of publication. In the fourth chapter on Don'ts for Electric Welders, welders are advised not to wear celluloid collars, as sparks from the arc may set them on fire and cause serious results. The author's view on fire hazard is perhaps inconsistent since only a few pages previously, a dimensional sketch is given of a welding screen made of three-ply wood. Again, a newcomer to welding might well gain the impression that it is common practice for welders nowadays to coat their own arc-welding electrodes, whereas in fact this necessity ceased to arise at least 20 years ago, much better results being obtained with the use of coated electrodes bought as such and made by specialists.

In recent years, many useful publications by the British Standards Institution have appeared on welding matters, but the most recent one referred to in the text was published in 1933. The authors have lost a valuable opportunity of putting this matter right in the present edition, and they might also have added information on argon-arc welding, submerged-arc welding, and automatic arc welding using covered electrodes. In general, it may be said that this book does not contribute usefully to existing literature on welding, and, indeed, may tend to mislead intending users and students as to the present state of the art.—A. J. HIPPERSON

CASSIE, W. FISHER, and J. H. NAPPER. "*Structure in Building.*" With a Foreword by W. A. Allen. 8vo, pp. 266. Illustrated. London, 1952: The Architectural Press. (Price 30*s.*)

Some 50 years ago architecture donned a cloak of artificiality beneath which the energies of architects were lost in a maze of ornamental chimney pots, stucco facades, and foibles of doubtful taste. Simultaneously the 20th century demand for large blocks of multi-storey buildings called for the services of structural engineers. A demand usually creates a means of solution and the timely arrival of rolled-steel sections and reinforced concrete firmly established the need for engineers in a field which had hitherto been the preserve of architects.

With these large buildings, which were in fact primarily engineering structures, proportions were dictated by functional requirements and stability computations. Once these were agreed upon, all that was left for the architect to do was to fill in the spaces between the structural members and to provide the services. This method of building undoubtedly produced serviceable blocks, but they were often of unimaginative design.

Some time about the middle twenties both architect and engineer understood the benefits which might accrue from closer co-operation. In France, Italy, and Germany many engineers complemented their qualifications by architectural studies—often with remarkable results.

"Structure in Building" attempts what is perhaps the next best solution, namely, to bring to the architect the essentials of structural design. The book, written jointly by an engineer and an architect, combines what is best in both professions, precision and style. It comprises ten chapters which deal with fundamentals, historical points, loading of structures, building materials, simple and redundant structures, foundations, deformations, new developments in materials and methods, and the means of selecting types of structure for particular purposes. In addition to numerous line diagrams, the book contains 68 remarkable plates illustrating significant timber, steel, and reinforced-concrete structures in many countries. The book has a very comprehensive index, which makes quick reference possible to any one of the numerous subjects dealt with, and contains chapter bibliographies to assist further reading. It is well written and very pleasingly produced.

In their preface, the authors mention that the book is primarily intended for architects and students. One might add that it should be of very considerable interest to civil engineers and to all who are interested in the science and art of building. If engineer and architect in the future can work as closely as Fisher Cassie and Napper have done in their book we may expect to see, one day, an increasing number of really fine buildings.—M. D. J. BRISBY

FUCHS, E., and H. BRADLEY. "*Welding Practice.*" Volume III. "*Welding of Non-Ferrous Metals.*" La. 4to, pp. xii + 183. Illustrated. London, 1952: Butterworth's Publications, Ltd. (Price 22*s.* 6*d.*)

Dealing specifically with the welding of non-ferrous metals, this volume is complementary to two others entitled, "Welding Methods and Tests" and "Welding of Ferrous Metals. It is emphasized in the preface that the intention is not to deal in textbook fashion with the subject matter but rather to meet the practical needs of those connected with welding. It was originally prepared for internal use in one of the large chemical organizations in Britain, and deals with those techniques and applications which are of current interest.

The clear and concise method of treating the information, which was evident in vol. 1, has been maintained, and the general impression created is one of extremely objective treatment of the practical matter rather than a vague accumulation of practical hints to the welder. It should appeal particularly to the designer, draughtsman, engineer, and foreman whose occupation is connected with welding.

There are 7 chapters dealing with the following subjects: Copper, brasses and bronzes, nickel and nickel-rich alloys, silver, aluminium and its alloys, lead, and brazing. Each chapter is built up around a common framework dealing specifically in each case with metallurgical factors, design information, welding materials, workshop practice, and special applications, and concludes with a bibliography. Abstruse metallurgical terms are carefully avoided, so that the more theoretical aspects covered can easily be assimilated by the practical man. Those terms which are not in general use in the shop have been selected from the text and listed at the end in a glossary in which they are very clearly explained. Perhaps a factor which has particularly great appeal is that the text is not a series of descriptions of how welding has been used for various applications, but aims rather at explaining the relative merits of each welding process and the reasons for using one technique or design feature in preference to another.

A surprisingly large section of the book is devoted to lead, and this may be found particularly helpful because so very little information is available on welding processes as applied to this particular material. The careful description of the equipment and technique used for lead burning, as the process of gas-welding lead has been erroneously called in the past, is of particular appeal to those engaged in the use of lead for such purposes as lining containers and equipment in contact with highly corrosive materials.

The final chapter on the brazing of ferrous and non-ferrous metals covers a wide range of materials and deals not only with brazing processes that are well established but also with processes of very recent origin such as induction brazing.

This publication contains a wealth of practical information on design and technique and is to the fore in its particular sphere.—A. J. HIPPERSON

GELEJI, A. "*Die Berechnung der Kräfte und des Kraftbedarfs bei der Formgebung im bildsamen Zustande der Metalle.*" First German edition. 8vo, pp. 248. Illustrated. Budapest, 1952: Akadémiai Kiadó.

The estimation of the forces involved in the plastic working of metals and the consequent design of suitable machinery tend to follow the tradition of observation and empirical data. In this book, however, the author, who is himself a design engineer, shows how practical design considerations in this field can be based on fundamental theoretical principles aided by the results of scientific research.

The German edition of this textbook, which was first published in Hungary in 1948, has been revised and expanded with the addition of comprehensive experimental data and an introductory chapter devoted to the basic principles governing the shaping of metals in the plastic state.

The author's prime interest is in rolling processes, and to this subject he devotes Chapters III and IV, comprising some 90 pages, dealing in considerable detail with design problems involving the rolling of bars, sheets, and tubes. The fundamental principles involved in forging and pressing operations, and the drawing of bars, tubes, and wire are discussed in Chapters II and V, respectively. In the latter chapter a useful expression is derived for the heat developed during cold-drawing. The extrusion process

in a press is briefly dealt with in Chapter VI and the loads required for the hot extrusion of commercial copper, brass, and aluminium are calculated. Problems connected with the bending of sheet and the deep-drawing of cups are discussed in Chapters VII and VIII, respectively.

The author has endeavoured to develop his methods of calculation with the express aim of conforming to the demands of design practice. Fully worked solutions to typical problems are appended to each chapter, and tables and diagrams are clearly presented.

This short book does not pretend to provide complete answers to all design problems covering the plastic working of metals; it does, however, offer practical solutions in a number of cases where no helpful answer can be obtained from the current technical literature.—P. FREEMAN

OSBORN, FRED M. "The Story of the Mushets." 8vo, pp. xii + 195. Illustrated. London, 1952: Thomas Nelson and Sons, Ltd. (Price 21*s*.)

The late Fred M. Osborn was, for the last years of his life, chairman of Samuel Osborn and Co., Ltd., of Sheffield, whose early success was due to the alloy tool steel 'RMS' (Robert Mushet's Special). Mr. Osborn himself had worked with Henry Mushet, Robert's younger son, and was thus a link in a chain of genius that joins today with the late XVIIIth century, when William Muschet gave up weaving in Dalkeith and opened an ironfoundry. This William, Mr. Osborn was able to establish to his own satisfaction, was descended from Gilbert Montfitchett, Duke of Brittany, who assisted his cousin William the Conqueror at Hastings. Through various modifications of name, and changes of fortune assisted by a family propensity for joining in unpopular causes, we come to the first great Mushet, David, son of William the ironfounder, author of the celebrated "Papers on Iron and Steel," and discoverer of the Black Band ironstone which, together with Neilsen's hot blast, gave such a great stimulus to Scottish iron production in the 1830–40's. Mr. Osborn shows clearly how David combined his studies of iron metallurgy with practical work in the industry, in those chapters which deal with his life at Coleford in the Forest of Dean. It was at Coleford that Robert Forester Mushet was born, and from the Forest that he got his unusual second name; he inherited likewise all his father's pioneering spirit and gift of language, and a good measure of the independence and courage of the Free Miners. Robert's contributions to the iron and steel industry are, first, the application of spiegeleisen, in the Bessemer process, and, secondly, the development of the first air-hardening alloy tool steel, 'RMS.' In the first case he undoubtedly suffered financial loss through the carelessness of the trustees who let his patents lapse, and he never gained quite the co-equal recognition with Sir Henry Bessemer that he felt was his due; nevertheless he was awarded the Bessemer Gold Medal of The Iron and Steel Institute for his services, and it was Bessemer who was partly responsible for the honour. In the second case, what he himself called "a patent mania" led him to the development of the high-carbon tungsten–manganese steels. This time, he took care, patent or no patent, not to lose the benefit of his discovery; the early stages of the manufacture of 'RMS' were carried out in tremendous secrecy at Coleford, and even when financial disaster overtook his own company, the Titanic Iron and Steel Co., Ltd., and he found it necessary to go into partnership with Samuel Osborn, the secrets were shared with few, and very trustworthy, persons indeed. The immense success of 'RMS' under the new company brought him prosperity at last and he retired to Cheltenham; but retired he might be, quiet he could not be. It was from peaceful Cheltenham that he conducted the controversy with W. T. Jeans that filled the pages of "Iron," "The Engineer," and "Engineering" for half of the year 1884, and established his claim to be, what Jeans had been loth to admit, one of the "Creators of the Age of Steel." The publication of Mr. Osborn's book, with its valuable assembly and marshalling of all the known and documented facts about Robert Forester Mushet, gives, once and for all, an independent verification of that great claim.—J. P. S.

PATERSON, E. V. "*Wire Rope Lubrication*." Sm. 8vo, pp. xii + 34. Illustrated. Wellington, Shropshire, 1952: Scientific Publications. (Price 3*s*.)

This is a small but useful publication which stresses the importance, both for safety and for long life, of the lubrication of wire ropes, especially in mine shaft and roadway haulage. Illustrations of the sections of complicated lays illustrate the difficulty, and the necessity, of ensuring that the lubricant penetrates fully, reducing friction between the strands and maintaining the flexibility of the core. Proprietary automatic lubricators are shown, as well as apparatus which can be contrived 'on the spot,' and employed as opportunity arises. A brief bibliography is attached.—J. P. S.

THE PHYSICAL SOCIETY. "*Reports on Progress in Physics*." Vol. XV (1952). 8vo, pp. iv + 338. Illustrated. London, 1952: The Society. (Price 50*s*.)

There is more of interest to the metallurgist in this volume of the series than in earlier ones, for the paper on "The Band Structure of Metals" which Dr. S. V. Raynor contributes, occupies nearly a quarter of the text. This is an intensive study, relating the electronic structure of metals to some of their more obvious properties, such as elasticity, and a number of monovalent and polyvalent metals are considered; greater difficulities arise with trivalent aluminium than with metals of lower valency, but, even here, the theory serves to explain the elastic anisotropy of this metal, and some of the phenomena encountered in aluminium-rich alloys can be interpreted. The extension of the theory to alloys of metals polyvalent with each other is considered difficult, and requiring further work. A subject of quasi-metallurgical interest treated in the volume is that of ferrites; the causes of the magnetic behaviour of these compounds of metallic oxides of which the lodestone is the first historical example, are discussed at length in an illuminating manner. A paper on "Turbulent Motion," besides summing up the advances in knowledge of this subject in the last few years, describes a number of new and elegant methods for observing it, which may be of interest to students of duct and of furnace design. The remainder of the volume, though of less interest to the metallurgist, maintains the high standard of the Society.—J. P. S.

SIMMONS, WARD F., and HOWARD C. CROSS. "*Report on the Elevated-Temperature Properties of Stainless Steels*." Issued under the Auspices of the Data and Publications Panel of the ASTM-ASME Joint Committee on Effect of Temperature on the Properties of Metals. Special Technical Publication No. 124. La. 4to, pp. iv + 116. Illustrated. Philadelphia, Pa., 1952: American Society for Testing Materials. (Price $4)

This report is a collection of data concerning the high-temperature strength of nine commonly used types of austenitic stainless steels including 18/8, 18/8 Ti, 18/8 Nb, 18/8 Mo, 25/20, and modifications. In 1938 a large book was published by the same organization dealing with all types of low-alloy and high-alloy steel; it is out-of-print and, in many cases, out-of-date, and this report is the first of a series to replace it section by section.

It fills a real need as a summary and collection of data on steels which, although U.S. in origin, are widely used in the rest of the world. Since it was drawn up at the request of various engineering bodies, however, it would perhaps have been better to have been more critical in editing. There is a large amount of scatter in many of the curves that may be most misleading to an engineer; similar steels apparently have a variation in strength of 3 to 1 at 100° C. The cause of the scatter may partly be due to the extensive extrapolation employed, many of the 100,000-hr. points being estimated from tests lasting only 1000 hr. Extrapolation is always needed in creep-strength determinations, but the average user will make most use of the summary graphs provided and will not appreciate the extent of the uncertainty. The data have been collected from 22 U.S. laboratories and there is a danger that some have not achieved the high standard of technique necessary for precision creep testing which is found in many of the U.S. laboratories. Some tests, for instance, are the result of stepping up stress or temperature and are therefore of doubtful value. The engineer must be careful, too, to take full note of the metallurgical condition of the steels tested. This can usually be found in the detailed results, but too many points are of little value because the heat-treatment is not known.

The scatter in the hot tensile proof-stress figures is particularly great, no doubt owing to variation in the strain rates, which are not quoted.

In spite of these criticisms a valuable service has been performed in drawing together a mass of data which have

not been available before in any country, and the remainder of the work will be awaited with interest by those who test and who use steels at elevated temperatures.—G. T. HARRIS

UNESCO. "*Index Bibliographicus.*" Directory of Current Periodical Abstracts and Bibliographies—Volume I, "*Science and Technology.*" Compiled by Theodore Besterman. La. 4to, pp. xiv + 52. Paris, 1952: UNESCO; London: H.M. Stationery Office. (Price 6*s.* 6*d.*)

This is the third edition of a compilation first made in 1925 by the Director of the Swiss National Library, and revised in 1931 with the assistance of the Director of the Prussian State Library. The present edition has been compiled on behalf of the International Federation for Documentation and is sponsored by the United Nations Educational, Scientific and Cultural Organization; it is therefore a really international publication. Users of older editions will not, whereas users of newer ones might, be misled by the title; the volume is an index only to those publications which regularly include abstracts or other bibliographical material, and not to *all* scientific and technical literature. Within this range, however, it seems complete enough, and each entry bears a coding which enables one to determine at a glance whether the abstracts are comprehensive or selective, indicative or informative, in what language they appear, and how many are printed per issue. The arrangement in subjects is according to the Universal Decimal Classification.—J. P. S.

NEW PUBLICATIONS

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BATES, L. F. "*Modern Magnetism.*" 3rd edition. Pp. xii + 506. Illustrated. London, 1951: Cambridge University Press. (Price 30*s.*)

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BRITISH IRON AND STEEL RESEARCH ASSOCIATION. "*Polarized Light in Metallography.*" Editors, G. K. T. Conn and F. J. Bradshaw. 8vo, pp. 130. Illustrated. London, 1952: Butterworth's Scientific Publications. (Price 21*s.*)

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"*Documentation Techniques in the U.S.A.: Selection, Reproduction, Dissemination.*" Report by a Group of European Experts. Pp. 61. Paris, 1951: Organisation for European Economic Co-operation; London: H.M. Stationery Office. (Price 4*s.*)

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"*French-English Science Dictionary.*" 2nd edition, edited by Louis DeVries. Pp. xii + 526. New York, 1951: McGraw-Hill Book Co. (Price $6.50)

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DE GROOT, S. R. "*Thermodynamics of Irreversible Processes.*" La. 8vo, pp. xvi + 242. Illustrated. New York, 1951: Interscience Publishers, Inc. (Price $4)

GROSSMANN, M. A. "*Elements of Hardenability.*" 8vo, pp. 164. Illustrated. Cleveland, Ohio: American Society for Metals. (Price $4.50)

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HOLMSTROM, J. E. "*Bibliography of Interlingual Scientific and Technical Dictionaries.*" Pp. 227. Paris, 1951: UNESCO. (Price 4*s.*)

HOSELITZ K. "*Ferromagnetic Properties of Metals and Alloys.*" Monographs on the Physics and Chemistry of Materials. 8vo, pp. xii + 317. Illustrated. Oxford, 1952: Clarendon Press. (Price 40*s.*)

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KLEDITZ, EMIL. "*Die Beschäftigung von Schwerbeschädigten in der Eisen- und Metallindustrie.*" Hrsg. vom Verband der Eisen- und Metall-Berufsgenossenschaften. Pp. 394. Illustrated. Berlin, Bielefeld, München, 1951: Erich Schmidt Verlag. (*Price* DM 24.–)

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LEHMANN, H. "*Metalle.*" Bd. I. "*Werkstoffprüfung.*" La. 8vo, pp. 360. Illustrated. Leipzig, 1951: Fachbuchverlag G.m.b.H. (Price DM 8.–)

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MINISTRY OF LABOUR AND NATIONAL SERVICE. "*Second Report of the Committee on the Safeguarding of Milling Machines.*" 8vo, pp. 36. Illustrated. London, 1951: H.M. Stationery Office. (Price 3*s.* 6*d.*)

OEHLER, G. W. "*Gestaltung gezogener Blechteile.*" Pp. 120. Illustrated. Berlin, Göttingen, Heidelberg, 1951: Springer-Verlag. (Price DM 8.40)

RITTER, FRANZ. "*Korrosionstabellen metallischer Werkstoffe,*" geordnet nach angreifenden Stoffen. 3., erw. Aufl. 8vo, pp. 283. Illustrated. Vienna, 1952: Springer-Verlag. (Price DM 34.50)

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